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Groundwater Pollution Transport from Tsumeb Copper Smelter in Namibia

master thesis

Author: Bc. Fredrika N. Shagama

Supervisor: doc. Ing. Naďa Rapantová, CSc.

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Student: **Bc. Fredrika Ndeutala Shagama**

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Groundwater Pollution Transport from Tsumeb Copper Smelter in Namibia

Description:

1. Introduction
2. Physical background of the area
3. Monitoring of groundwater pollution
4. Geochemical and transport processes, prediction of contaminant plume movement
5. Conclusions

References:

Extent and terms of a thesis are specified in directions for its elaboration that are opened to the public on the web sites of the faculty.

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prof. Ing. Ctirad Schejbal, CSc.
Head of Institute

prof. Ing. Vojtech Dimer, CSc.
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Bc. Fredrika N. Shagama: Groundwater Pollution Transport from Tsumeb Copper Smelter in Namibia

Summary

The master thesis “Groundwater Pollution Transport from Tsumeb Copper Smelter in Namibia” firstly presents the physical conditions of the Tsumeb area i.e. the description of the study area, climatology, geomorphology, geology and hydrogeology. The subsequent part after physical conditions is the monitoring of groundwater quality on the site. Furthermore, the thesis focuses on the general geochemical and transport processes that control the behavior of arsenic in the environment. A geochemical transport model PHREEQC was used to calculate aqueous geochemical reactions. The second last subchapter deals with the prediction of the contaminant plume movement based on the model outputs, which is the primary objective of this thesis.

Keywords: Groundwater; pollution; Tsumeb Smelter; geochemical processes; transport processes; arsenic; geochemical model; contamination plume; PHREEQC.

Anotace

Diplomová práce "Transport znečištění podzemních vod z Tsumebské měděné hutě v Namibii" představuje fyzikální podmínky oblasti Tsumeb tj. popis studované oblasti, klimatologie, geomorfologie, geologie a hydrogeologie. Následná část se zabývá monitorováním stavu znečištění podzemních vod v zajmové oblasti. Dále se práce zaměřuje na obecné geochemické a transportní procesy řídící chování arsenu v životním prostředí. Geochemický transportní model PHREEQC byl použit k výpočtu vodných geochemických reakcí. Předposlední podkapitola se zabývá predikcí pohybu kontaminačního mraku na základě výsledků z modelu PHREEQC, což je hlavním cílem této práce.

Klíčová slova: Podzemní voda; znečištění; tsumebská huť; geochemické procesy; transportní procesy; arsen; geochemický model; kontaminační mrak; PHREEQC.

2015

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List of Abbreviations

DPMT- Dundee Precious Metals Tsumeb (The Tsumeb Smelter)

ESE-WNW- East-Southeast to West-Northwest

ESIA- Environmental and Social Impact Assessment

GCS- Groundwater Consulting Services

mamsl- meters above mean sea level

mbgl- meters below ground level

mg/l- milligram per liter

MME- Ministry of Mines and Energy (Namibia)

NCS- Namibia Custom Smelters

OML- Otavi Mountain Land

SDWF- Safe Drinking Water Foundation

U.S. EPA- United States Environmental Protection Agency

WHO- World Health Organization

1 Introduction and Objectives

Groundwater pollution occurs when hazardous substances come into contact and dissolve in the water that has infiltrated into the soil. This type of pollution can be of natural or anthropogenic origin. Groundwater can become contaminated in many ways. For instance, if rain water or surface water comes into contact with contaminated soil while seeping into the ground, it can become polluted and can carry the pollution from the soil to groundwater. Some liquid hazardous substances do not mix with the groundwater, but remain pooled within the soil or bedrock. These pooled substances can act as long-term sources of groundwater contamination as the groundwater flows through the soil or rock and comes into contact with them (U.S. EPA, 2011).

According to SWDF (2009), the water quality is impacted by the following mining activities:

- Acid Rock Drainage (ARD): is a natural process whereby sulphuric acid is produced when sulphides in rocks are exposed to air and water. Acid Mine Drainage (AMD) is essentially the same process, greatly magnified. When large quantities of rock containing sulphide minerals are excavated from an open pit or opened up in an underground mine, it reacts with water and oxygen to create sulphuric acid. When the water reaches a certain level of acidity, a naturally occurring type of bacteria called Thiobacillus ferroxidans may kick in, accelerating the oxidation and acidification processes, leaching even more trace metals from the wastes. The acid will leach from the rock as long as its source rock is exposed to air and water and until the sulphides are leached out, a process that can last hundreds, even thousands of years. Acid is carried off the mine site by rainwater or surface drainage and deposited into nearby streams, rivers, lakes and groundwater. AMD severely degrades water quality, and can kill aquatic life and make water virtually unusable.
- Heavy metal contamination and leaching: heavy metal pollution is caused when such metals as arsenic, cobalt, copper, cadmium, lead, silver and zinc contained in excavated rock or exposed in an underground mine come in contact with water. Metals are leached out and carried downstream as water

washes over the rock surface. Although metals can become mobile in neutral pH conditions, leaching is particularly accelerated in the low pH conditions such as are created by Acid Mine Drainage.

- Processing chemicals pollution: This kind of pollution occurs when chemical agents (such as cyanide or sulphuric acid used by mining companies to separate the target mineral from the ore) spill, leak, or leach from the mine site into nearby water bodies. These chemicals can be highly toxic to humans and wildlife.

Furthermore, residential, municipal, commercial, industrial, and agricultural activities also cause groundwater contamination which affect the quality of groundwater. According to U.S. EPA (2012), contaminants may reach ground water from activities on the land surface, such as releases or spills from stored industrial wastes; from sources below the land surface but above the water table, such as septic systems or leaking underground petroleum storage systems; from structures beneath the water table, such as wells; or from contaminated recharge water.

Depending on groundwater physical, chemical, and biological properties, a contaminant that has been released into the environment may move within an aquifer in the same manner that groundwater moves. It is possible to predict, to some degree, the transport within an aquifer of those substances that move along with groundwater flow. For example in shallow subsurface, both water and certain contaminants may flow in the direction of the topography slopes from recharge areas to discharge areas (U.S. EPA, 2012).

The health effects from groundwater pollution depend on the type of pollutants and its concentration in the water, the period at which the individual has been exposed to the pollutant(s) and so on. Pollution from groundwater often causes diarrhea and stomach irritation, which can lead to more severe health effects. Accumulation of heavy metals like arsenic and some organic pollutants can lead to cancer, birth defects, reproductive abnormalities and other severe health effects.

1.1 Copper Production and Groundwater Pollution

Copper production is not an environmentally benign activity. All aspects of its (copper) production from mining and leaching to milling, smelting, refining and electrowinning can have significant adverse impacts on air quality, surface and groundwater quality, and the land. While these impacts can be severe when the materials handled include toxic or hazardous substances e.g. ores with a relatively high concentration of arsenic (U.S. Congress, Office of Technology Assessment, 1988).

Smelting is the process of separating a metal of interest from impurities by heating the concentrate to a high temperature to cause the metal to melt. Smelting the concentrate produces a metal or a high-grade metallic mixture with a large quantities of solid waste known as slag, which usually contains significant amount of contaminants. Metal-bearing dust particles can travel far distances to pollute the soil and surface waterways. Highly alkaline smelter effluent and tailings also release acid to waterways from waste pits. Arsenic, lead, and cadmium are the metals of concern most commonly associated with copper ores. These toxic metals can accumulate in the environment and concentrate in the food chain, reaching levels that are toxic to both human and aquatic life (U.S. Congress, Office of Technology Assessment, 1988).

The principal sources of pollution caused by smelting are contaminant-laden air emissions and process wastes such as waste water and slag. The smelting of sulfide ores results in the emission of sulphur dioxide gases, which reacts chemically in the atmosphere to form sulphuric acid mist. As this acid rain falls to the earth surface, it increases the acidity of soils, streams, rivers, and lakes. The same water from these surface water sources will eventually reach grondwater through seepage, which affects groundwater quality.

Since the impacts of groundwater pollution is a global concern, it should be a matter of public health and definitely of scientific interest in order to tackle it.

When groundwater becomes contaminated, it is difficult and expensive to clean up. To begin to address pollution prevention or remediation, we must understand how surface waters and groundwaters interrelate. Groundwater and

surface water are interconnected and can be fully understood and intelligently managed only when that fact is acknowledged. If there is a water supply well near a source of contamination, that well runs the risk of becoming contaminated. If there is a nearby river or stream, that water body may also become polluted (U.S. EPA, 2012).

Due to the above mentioned general adverse impacts smelting processes have on groundwater, most if not all, smelters in the world have set up groundwater monitoring programs. These programs serve as a "tracking" body which operates throughout the smelter's lifetime and for some time after the operations in order to keep track of possible contaminant concentrations and their movement in the environment, particularly groundwater.

1.2 An Outline of Tsumeb and the Smelter

The town of Tsumeb is located at 19º 15’ S and 17º 42’ E and it lies 1320 m above sea level. Tsumeb is the capital of Oshikoto Region, located in the northern central part of Namibia (see Figure 1-1) and approximately 430 km north of the capital city, Windhoek. The Tsumeb Smelter is located adjacent to the town of Tsumeb in the Oshikoto Region of Namibia, approximately 2km north east of the town centre.

Figure 1-1 Location of study area, marked by the red star (DPMT, 2012)

1.2.1 Smelter Operations

Most of Namibia's known copper and lead deposits are Tsumeb-type, Besshi-type or Red Bed-type. Currently the only copper producer in Namibia is Ongopolo Mining and Processing Ltd. Ongopolo mines a Besshi-type cupriferous pyrite ore from the recently opened Matchless Mine Western Extension (1.35 Mt ore at 2.12% copper), situated some 30 km west of Windhoek, and from the Otjihase Mine (Resource of 12 Mt at a grade of 1.9% copper), situated 30 km east of Windhoek. Copper concentrate is transported via rail from the Otjihase Mine to the Tsumeb Smelter to produce blister copper. Other Tsumeb-type copper-lead

deposits investigated during recent years include the new Tsumeb West Mine, Asis Far West Mine (inferred mineral resource of 3 Mt at a grade of 2.5% copper), Khusib Springs Mine (245 000 t at a grade of 4.5% copper, 1.15% lead, 1.43% zinc and 350 ppm silver) and the Tschudi deposit (resource of 43 Mt at a grade of 0.85% copper, stripping ratio 1:6), all situated on the carbonate platform of the Otavi Mountainland. The copper Smelter in Tsumeb receives copper concentrate not only from Ongopolo-owned mines in Namibia, but from Zambia, Chile, South Africa and Zimbabwe. Potential exists to identify and develop new deposits as well as to re-evaluate known deposits (MME Namibia, 2015).

The copper smelter has been in operation for over forty years, under various owners. From 24 March 2010, the smelter is owned and operated by Dundee Precious Metals Inc. (also referred as Dundee Precious Metals Tsumeb, or DPMT) formerly owned by Namibia Custom Smelters (Proprietary) Limited, or NCS. That same year, Dundee Precious Metals completed the acquisition of NCS, a metals processing and smelting operation (the "Smelter") from Weatherly Mining International by way of the purchase of 100% of the shares of NCS (DPMT, 2012).

Figure 1-2 and Figure 1-3 show the satellite view of the Tsumeb Smelter and the partial view of its infrastructure from the south, respectively. The site is situated in a local valley with hills towards the south and north of the site and Figure 1-4 shows the view of the Smelter from the East.

Figure 1-2 Satellite view of the Smelter (Google earth, 2015)

Figure 1-3 Tsumeb Smelter Complex, general view from the South (Google earth, 2015)

Figure 1-4 The Smelter complex view from the East (Van Rooyen and Nel, 2013)

According to DPMT (2012), the smelter was constructed in the early 1960s to process concentrate from the Tsumeb copper mine and is one of only five commercial-scale smelters in Africa. The smelter is one of only a few in the world which is able to treat arsenic and lead bearing copper concentrates and is therefore able to conclude long term favorable contracts to treat such concentrates. Both blister copper and arsenic trioxide (As_2O_3) are produced from the concentrates. The blister copper is delivered to refineries for final processing and the As_2O_3 (final by product) is sold to third party customers. Tsumeb Smelter has become a major custom smelter with brown-fields expansion potential. It produces blister copper (98.5% Cu) and has the ability to treat complex copper concentrates.

1.2.1.1 Arsenic plant

Concentrates and other secondary material processed at the Tsumeb Smelter are traditionally relatively high in arsenic. The arsenic passes through the smelter and is captured from the off-gases in the bag houses. Bag house dusts with high arsenic levels are used as feedstock into the arsenic plant. Figure 1-5

shows a bag house where the proposed new acid plant would be located. Bag house dusts that cannot be processed in the arsenic plant are disposed of in the waste disposal site. The arsenic plant is used to produce arsenic trioxide from dusts recovered during the smelting process. Four single hearth Godfrey roasters are used to convert the material into arsenic trioxide, which is sold for the manufacture of pesticides and wood treatment (DPMT, 2012).

Figure 1-5 Proposed site of new acid plant where the old bag house currently stands (Golder Associates, 2013)

1.2.1.2 Slag mill

According to DPMT (2012), slag skimmed from the various furnaces is granulated in water and passed to the slag mill for screening, milling and concentration of copper by conventional flotation. The over sized material is crushed and returned to the milling circuit for processing. The concentrates

produced are re-incorporated into the smelting process. Slag mill tailings are placed on the old tailings dam to the west of the smelter. Water from the tailings dam is used in the smelter for slag granulation and dust suppression.

1.2.1.3 Mill tailings dam

Historically under Tsumeb Corporation Ltd. operations, the tailings originating from the slag mill were deposited north of the slag mill adjacent to the access road to the Smelter. The tailings however still contain pay metals including copper and it is likely that the dump will be reprocessed in order to recover these metals. A new tailings dam to the east of the smelter was also used to deposit slag mill tailings – this unit would undergo rehabilitation (DPMT, 2012). The slag mill tailings located in the northeastern part of the site are shown in Figure 1-6.

According to Van Rooyen and Nel (2013), the complex arsenate slag produced between 1907 and 1948 could readily dissolve during the rainy seasons, leaching As at hazardous concentrations (4 mg/l) into the environment. Runoff water from the slag contained 6 mg/l As and the return water pond contained 16 mg/l As. Surface water runoff controls at the site seem to have been breached at times, causing contaminated water to flow away from the site and potentially recharge the aquifers. For the contaminant transport it is assumed that the site was well managed during the 3 main operational phases. Surface runoff from the dumps was probably contained in the return water dams during these periods. It is assumed that the site management was not done between the different operational phases. Surface water runoff would therefore not be contained on the site and allowed to flow off site.

Figure 1-6 Southern edge of the slag mill tailings dam located adjacent to the northeastern part of the Smelter Complex (Kříbek et al., 2005).

Contaminants currently related to the site include more than 100 years of smelter operations with 2 tailings dams and various storage areas for slag and calcine. It seems that runoff from the site has at times flowed off the site and ponded away from the site, acting as additional; sources of groundwater contamination (Nel, 2014).

The sources of groundwater pollution in the Smelter are; tailings dumps, the return water dam (tailing ponds) and possibly, the arsenic dust dumpsite. Contaminants from tailing dumps leach into groundwater through rainwater infiltration into the ground. Return water dam allows contaminants constituted in the waste water to reach groundwater by infiltration through its bases or side-walls, since the dam is said to be unlined. The arsenic dust dumpsite, where arsenic dust bags are deposited is located on the southern west of the Smelter.

The base of the dumpsite was said to be lined, but it may not last long enough to prevent the leaching of arsenic dust into groundwater.

1.2.2 Land Use and Vegetation in the Smelter Area

The Tsumeb vegetation is classified as dry woodland and savanna. The district is suitable for intensified farming and crop production, especially with high yielding dolomitic resources available in places, enabling the use of centre pivot irrigation. Commercial agriculture is restricted to a few farms to the north-east and east of Tsumeb. Farmers in the area grow citrus fruits with much success. The main crops grown are maize, sorghum and sunflowers (Van Rooyen and Nel, 2013).

1.3 Thesis Objectives

Tsumeb Smelter, like many other smelters in the world produces waste materials that pose great risks to the environment around it, particularly groundwater pollution which mostly lead to serious health and environmental problems. The main objective of this thesis is to predict the movement of the contaminant plume (from the source in the direction of groundwater flow) from Tsumeb Smelter in Namibia with the main focus on Arsenic, the major contaminant of concern and other possible minor contaminants on site.

2 Physical Background of the Area

The Tsumeb region forms part of the Otavi Mountain Land which has been classified into Mountain Savanna and Karstveld. Summit areas attain heights of 1300 to 1400 m above sea level, the bottom of intermontane basins are located at an altitude from 1220 to 1230 m. The Karstveld landscape extends as narrow, raised margin that encircles the lower-lying Owambo Basin in the central northern Namibia. There are no major river systems in the Tsumeb region. However, the only one permanent stream in the Tsumeb region is represented by the Jordan Creek, which springs south of Tsumeb and terminates in a swampy delta area north of the town (Nunes, 2007).

2.1 Climatology

The climate and land use plays an important role in assessing the dominant groundwater recharge mechanisms. Tsumeb has a humid subtropical climate with very hot summers and mild winters. It borders on a semi-arid climate and the mean temperature at Tsumeb is 22°C. The average annual precipitation is 566 mm per year with volumes of less than 300 mm per year and above 1000 mm per year not uncommon. The mean annual evaporation ranges between 2600 to 2800 mm per year (Van Rooyen and Nel, 2013).

Petrie (2013) described the rainfall as highly erratic and mainly occurs during the summer months between November and March. Higher rainfall is encountered in the most elevated areas of the Otavi Mountain Land in the south of the study area. The expected low runoff rates and higher recharge in the Otavi Mountain Land provide favorable recharge zones for the regional aquifer.

The annual rainfall recorded for a period of 84 years (from the year 1911 to 1995) is shown by the graph image in Figure 2-1.

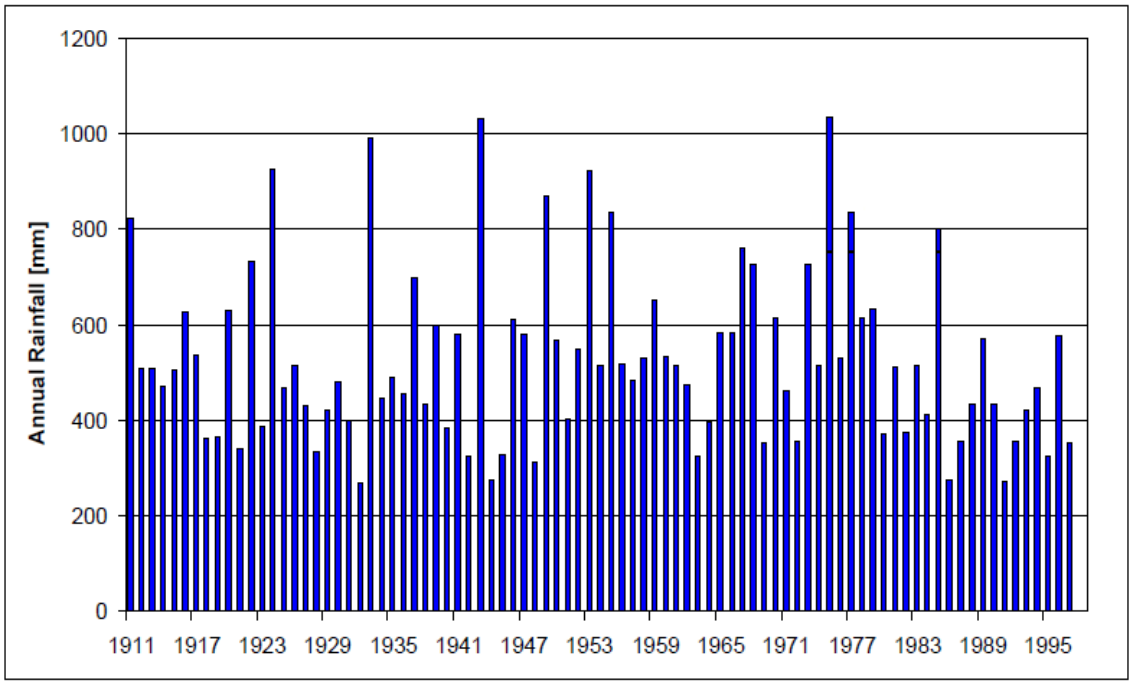


Figure 2-1 Recorded annual rainfall of Tsumeb from 1911 to 1995 (Van Rooyen and Nel, 2013)

Figure 2-2 shows rainfall data aggregated in the past 95 years from 1914 to 2009. From the graph is can be seen that, mean monthly rainfall has not fluctuated much in these years. The evaporation rate distributed on a monthly basis in proportion to mean monthly temperatures and the net monthly mean evaporation rate from the year 1914 to 2009 are shown in Figure 2-3 and Figure 2-4 respectively.

Figure 2-2 Graph showing Mean monthly rainfall over the past 100 years (Petrie, 2013-edited)

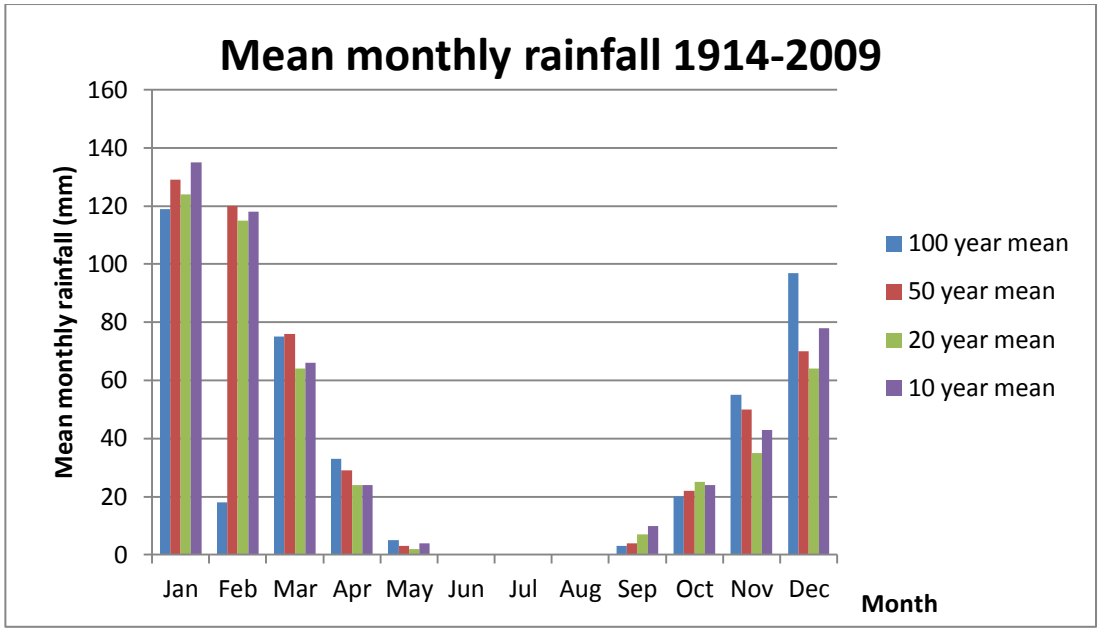


Figure 2-3 Graph showing Mean monthly evaporation (Petrie, 2013-edited)

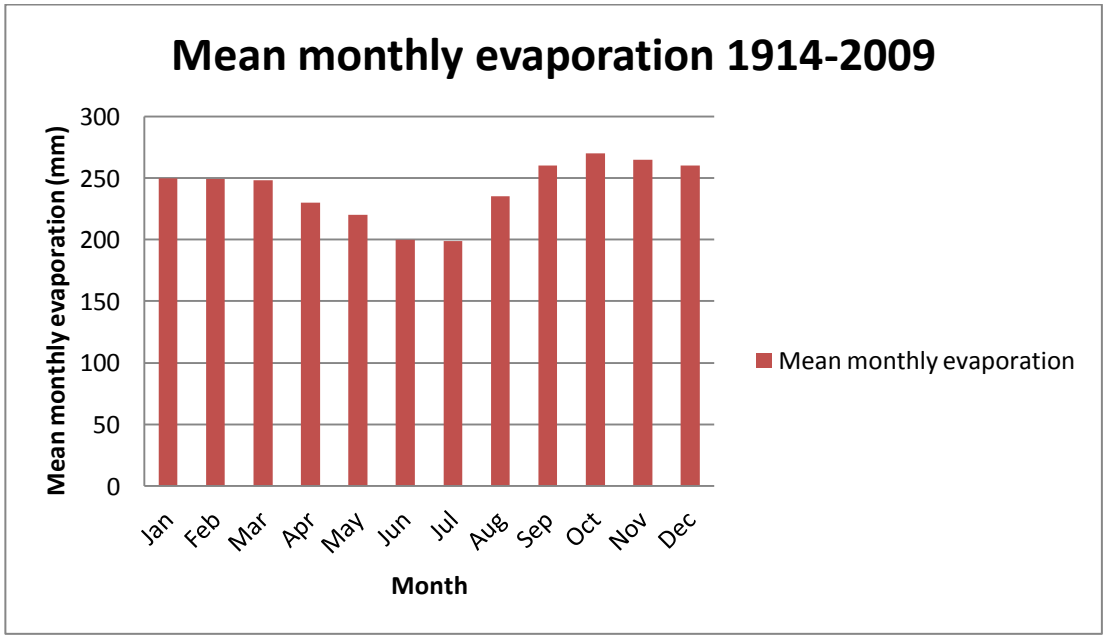
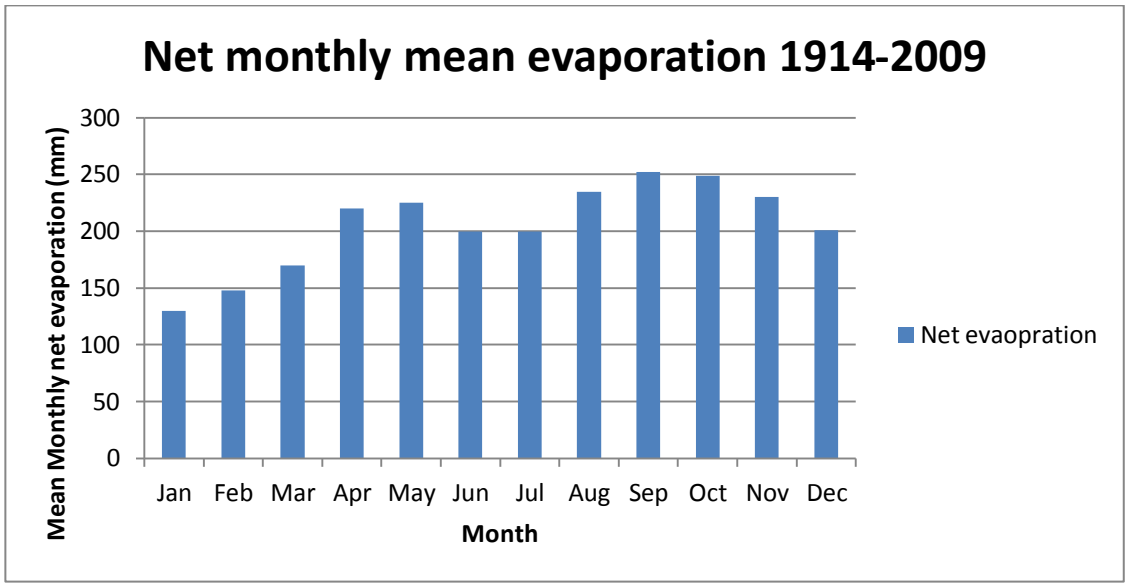


Figure 2-4 Graph showing Mean Monthly net evaporation (Petrie, 2013-edited)



2.1.1 Geomorphology

The Tsumeb region forms a part of the northern flanks of the Otavi Mountains, composed of Neoproterozoic limestones and dolomites with schist intercalation. Numerous karst phenomena (scrap, sinkholes) are characteristic for carbonate-dominated landscape. Summit areas attain heights 1 300 to 1 400 m above sea level, the bottom of intermountain basins are located at an altitude from 1220 to 1230 m (Kříbek et al., 2005). The position of Tsumeb on the Namibian map of elevations and relief is shown in Figure 2-5 (area in the map is enclosed by the red ellipse).

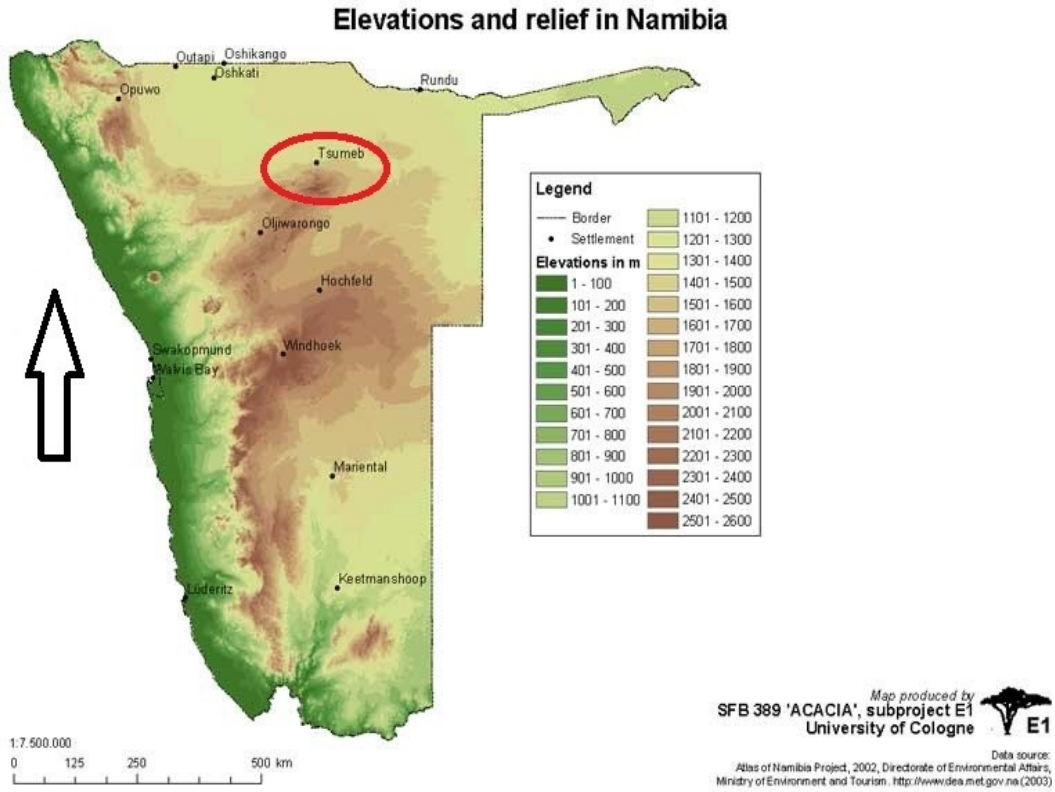


Figure 2-5 Map of Elevations and relief in Namibia (Digital Atlas of Namibia, 2002-edited)

2.2 Geology

2.2.1 An Outline of the Regional Geology of Namibia

The geology of Namibia is dominated by three large-scale metamorphic belts, which are the result of Neoproterozoic continental collision between the Kalahari and Congo Cratons in Africa and the Rio de la Plata Craton of South America. The northernmost tip of the Gariep belt is exposed in southern Namibia, whereas the Damara and Kaoko belts represent two major metamorphic belts exposed in central and northwestern Namibia, respectively (Kříbek et al., 2005).

The general geological map of Namibia with geological division is illustrated in Figure 2-6 with the geological situation of the area of interest in the red ellipse.

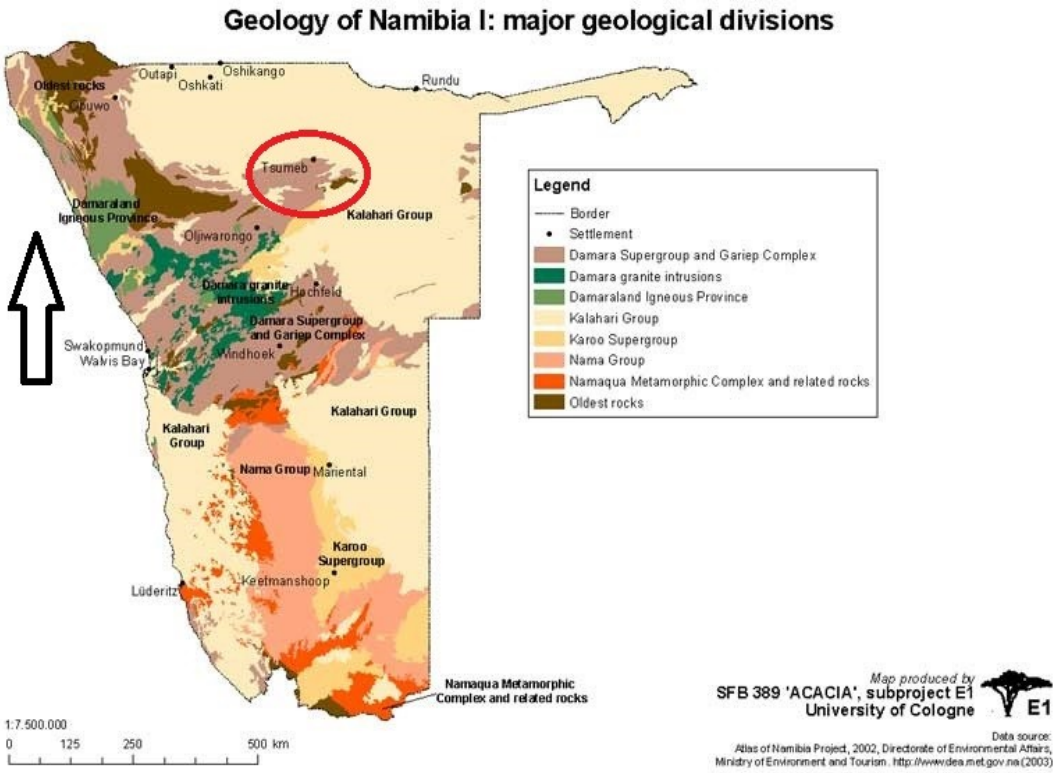


Figure 2-6 Major geological divisions in Namibia (Digital Atlas of Namibia, 2002-edited)

The Otavi Mountainland (OML) lies on the northern platform (shelf) area of the Otjiwarongo branch of the Damara Orogen. The granite and gneiss of the Grootfontein Basement Complex are overlain with sediments of the northern facies of the Damara Sequence consisting of a basal arenaceous unit, middle carbonate unit (Otavi Group) and an upper clastic unit. Within the lower Otavi Group (Abenab Subgroup) intermittent layers of quartzite, tillite, marble and shale have a low permeability. The dolomitic rocks from the Otavi Group have been stratigraphically altered into several synclines and anticlines trending in a general west-east direction (Van Rooyen and Nel, 2013). Figure 2-7 illustrates a geology map of Namibia with geological groups (with study area enclosed by the red circle/ellipse on the map).

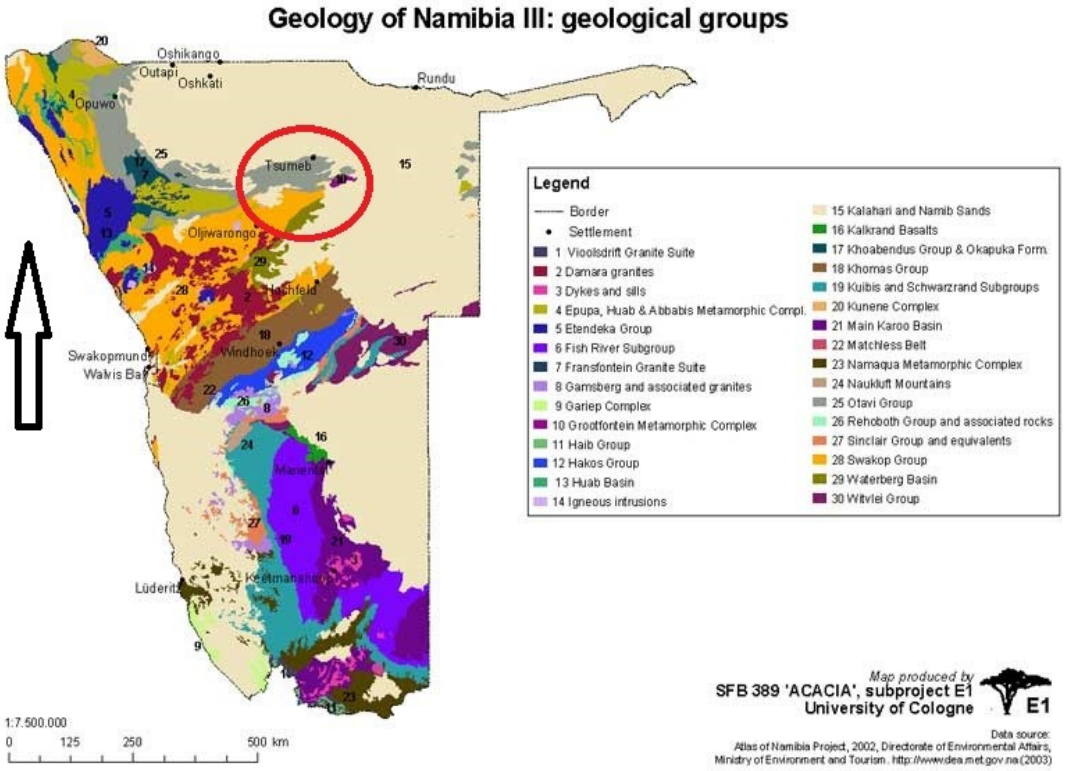


Figure 2-7 Map of geological groups in Namibia (Digital Atlas of Namibia, 2002-edited)

The Karoo Sequence (towards the north of Tsumeb) was deposited in the basin throughout the Permian and the Mesozoicperious periods. The Karoo is overlain by the Tertiary and Quaternary sediments of the Kalahari Sequence. The thickness of the Kalahari Sequence forms an extensive cover of terrestrial origin and amounts to some tens of metres and seldom exceeds 200 m in the northern part of the basin (Van Rooyen and Nel, 2013).

The map in Figure 2-8 shows the detailed regional geological map around the Tsumeb area. The site area (Smelter) is marked by a small yellow polyline in the latter figure. The area surrounded by light green polyline indicated as "Model extent" appears in the image, because the map image was obtained from a different study that dealt with modeling of the site and it was impossible to remove it for this work.

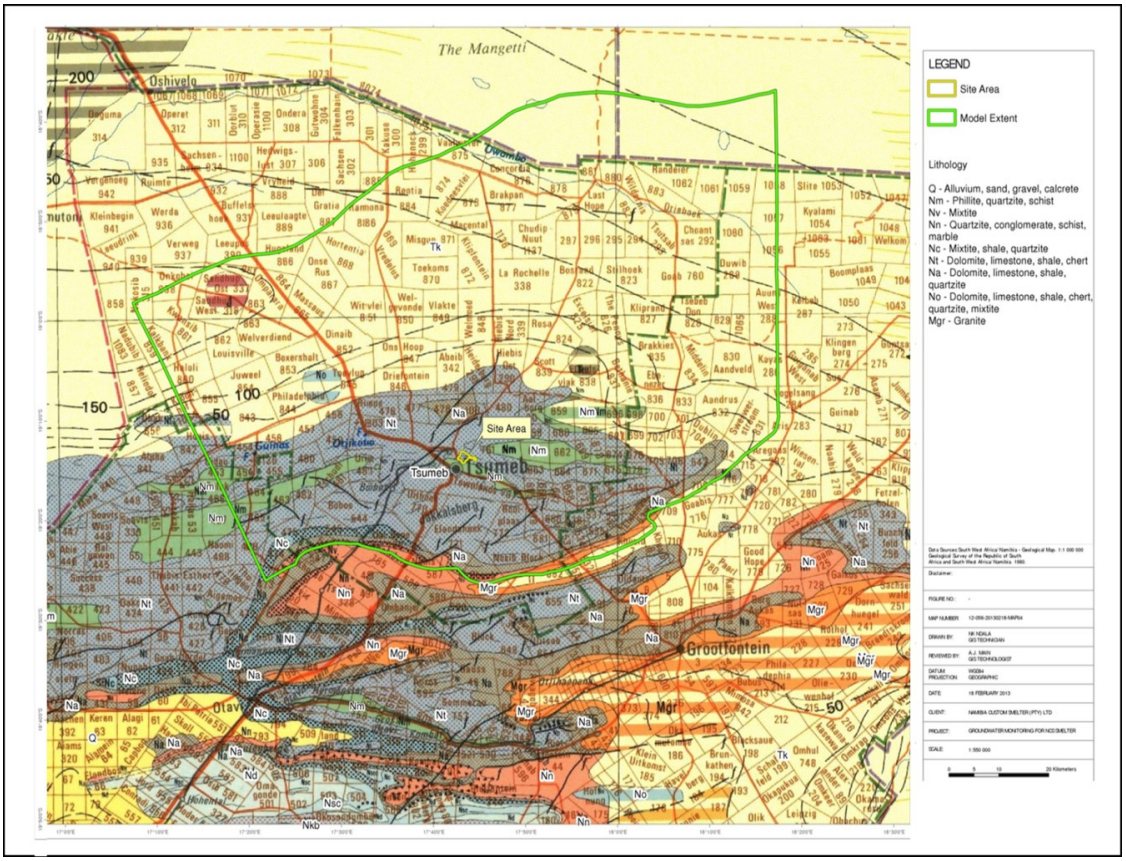


Figure 2-8 Regional Geology map (Van Rooyen and Nel, 2013)

Table 2-1 Stratigraphic Succession for Otavi Mountain Land regional geology (Van Rooyen and Nel, 2013-edited)

System	Sequence	Group	Subgroup	Formation	Lithology	Average thickness
Quaternary					Aeolian sands	
				Andoni	Sands, clay, calcrete	
		Kalahari		Olukonda	Sands,calcrete	
Tertiary				Beiseb	Gravel, sandstone	
Cretaceous Jurassic Triassic	Karoo 280 Ma			**Unconformity**		
				Undifferentiated Etjo/Etendeka/Dwyka and equivalent	Sandstone, shale, basalt, dykes	
Permian to Cambrian						
	Unconformity (280-450 Ma)					
		Mulden (570-650 Ma)		Tschudi	Shale, phyllite, siltstone, sandstone, conglomerate	>700 m
Namibian	Damara	**Unconformity (570-650 Ma)**				
		Otavi (700-730 Ma)	Tsumeb	Huttenberg	Dolomite, shale, chert	840 m
				Elandshoek	Dolomite	<1200 m
				Maieberg	Dolomite, limestone, shale beds	880 m
				Chuos	Quartzite, tillite, shale	200 m
			Unconformity			
			Abenab	Auros	Dolomite, limestone, mart, shale	350 m
				Gauss	Dolomite	750 m
				Berg Aukas	Dolomite, limestone, shale	550 m
		Unconformity (830-840 Ma)				
		Nosib (900 Ma)		Gaub	Phyllite, tuff, quartzite	
				Nabis	Quartzite, conglomerate	750 m
Mokolian		**Unconformity (950-1500 Ma)**				
		Grootfontein Basement complex			Granite, gneiss, schist	

The early phase of the Damara Orogen was characterised by intracontinental rifting and continental erosion. The Nosib Group (clastic

sediments) were deposited in the rift and erosion valleys. The further drifting apart of the continental plates eventually created oceans between the Congo Craton in the north and the Kalahari Craton in the south. Deposits of mainly dolomite and limestone accumulated on the shelf that formed on the southern edge of the northern craton, which today is the Cuvelai-Etosha Basin (Van Rooyen and Nel, 2013).

During the Late Precambrian age (~650 - 630 Ma) the direction of the crustal movement has reversed and the Damaran Mobile Belt was pushed under the Congo Craton plate. As a result from the continental collision and the subduction of the oceanic crust the dolomite and limestone along the edge of the Cuvelai-Etosha Basin were intensely folded and tilted upwards. Tsumeb is situated at the rim of the dolomite and limestone Cuvelai-Etosha Basin.

According to Van Rooyen and Nel (2013), the Tsumeb deposit contains a wide variety of lead, copper and zinc ores. In addition silver, arsenic, antimony, cadmium, cobalt, germanium, gallium, iron, mercury, molybdenum, nickel, tin and vanadium occur. The ore-body forms a steep sub-vertical pipe-like structure (channel), with a depth of approximately 1,800 m. The sturcture is sited on a narrow zone of folding and is defined by rock alteration and faulting. Deep solution caverns in the Otavi Group formed through the circulation of meteoric waters below the eroding surface. Prior to the folding event the caverns were filled with unconsolidated sediments similar to sediments of the Tschudi Formation which were deposited on top.

Indications are that, the geology in the regional area is structurally controlled with folding being the major structural mechanism as well as faulting. North East-South West trending faults are naturally compressional or closed fractures and only when doleritic dykes intrude this structural regime, will the fractures become more open and expected to carry water. There are dykes and dyke swarms with extensions of several kilometres present within the site area. These dykes are of doleritic nature from the Karoo Sequences and roughly follow a south west-north east direction (Van Rooyen and Nel, 2013).

2.2.2 Geology of the Tsumeb Area

The Tsumeb deposit is hosted in dolomites and limestones of the Otavi fold belt (Figure 2-9). Here, sedimentation on the Congo Craton started by the deposition of the basal conglomerates and quartzites of the Nosib group. Marbles and schists of the Swakop group are missing in this part of the Congo Craton cover and members of the Nosib group are directly overlain by a thick sequence of shelf carbonates of the Otavi group. The Otavi group is subdivided into two sub-groups:

1) *The Abenab sub-group* consists mostly of laminated dolomites in the lower part, and of intercalating bedded limestone and shale with massive dolomites in the upper part.

2) *The Tsumeb sub-group* is composed mostly of limestones and dolomites with horizons of spectacular diagenetic chert in the uppermost part of the unit (Kříbek et al., 2005)

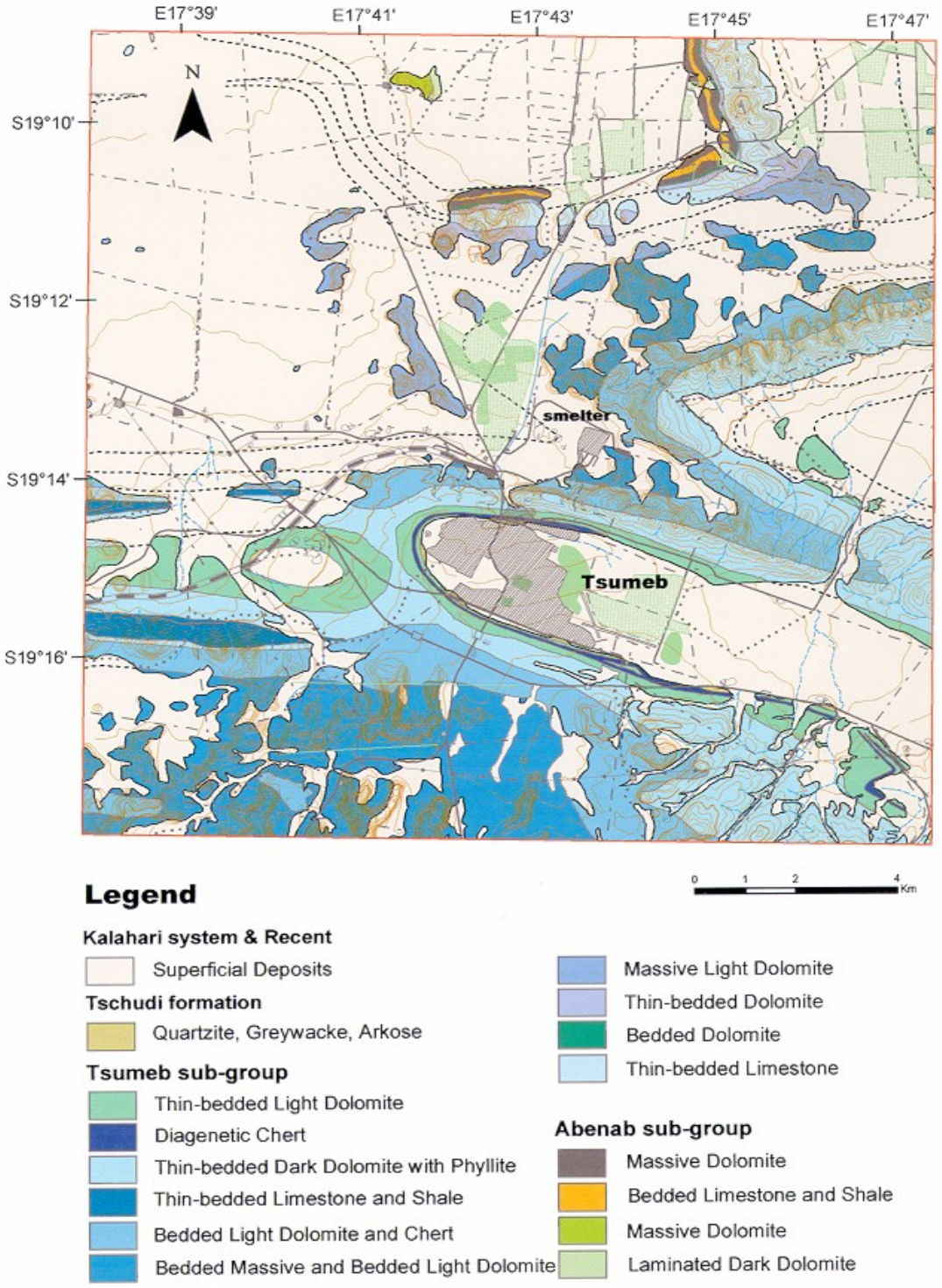


Figure 2-9 Simplified geological map of the Tsumeb area (Kříbek et al., 2005)

The stratigraphic setting of the NCS Smelter is shown in Figure 2-10, with details of the stratigraphy in the smelter area in Table 2-2. The Smelter (NCS) site is situated on dolomitic rock of the Tsumeb Subgroup (mostly lithozone T5) in an ESE-WNW sloping valley formed as part of an anticline between two synclines, with the site positioned between two synclines.

Various lineaments from the ASTER satellite image interpretation are passing through or close to the site. These lineaments can be zones of high hydraulic conductivity and form preferential pathways to contaminant movement (Van Rooyen and Nel, 2013).

The North Break can be important as it is a zone of alteration situated within the bedding of the lower part of the T6 unit, a section which is rich in stromatolite beds. The zone of alteration is restricted to a stratigraphic width of 10m within which lenses of partly brecciated, altered dolomite may reach a thickness of 4m. Surface exposures show that solution collapse breccia has formed at several places above the North Break, locally extending upward into the T8 unit.

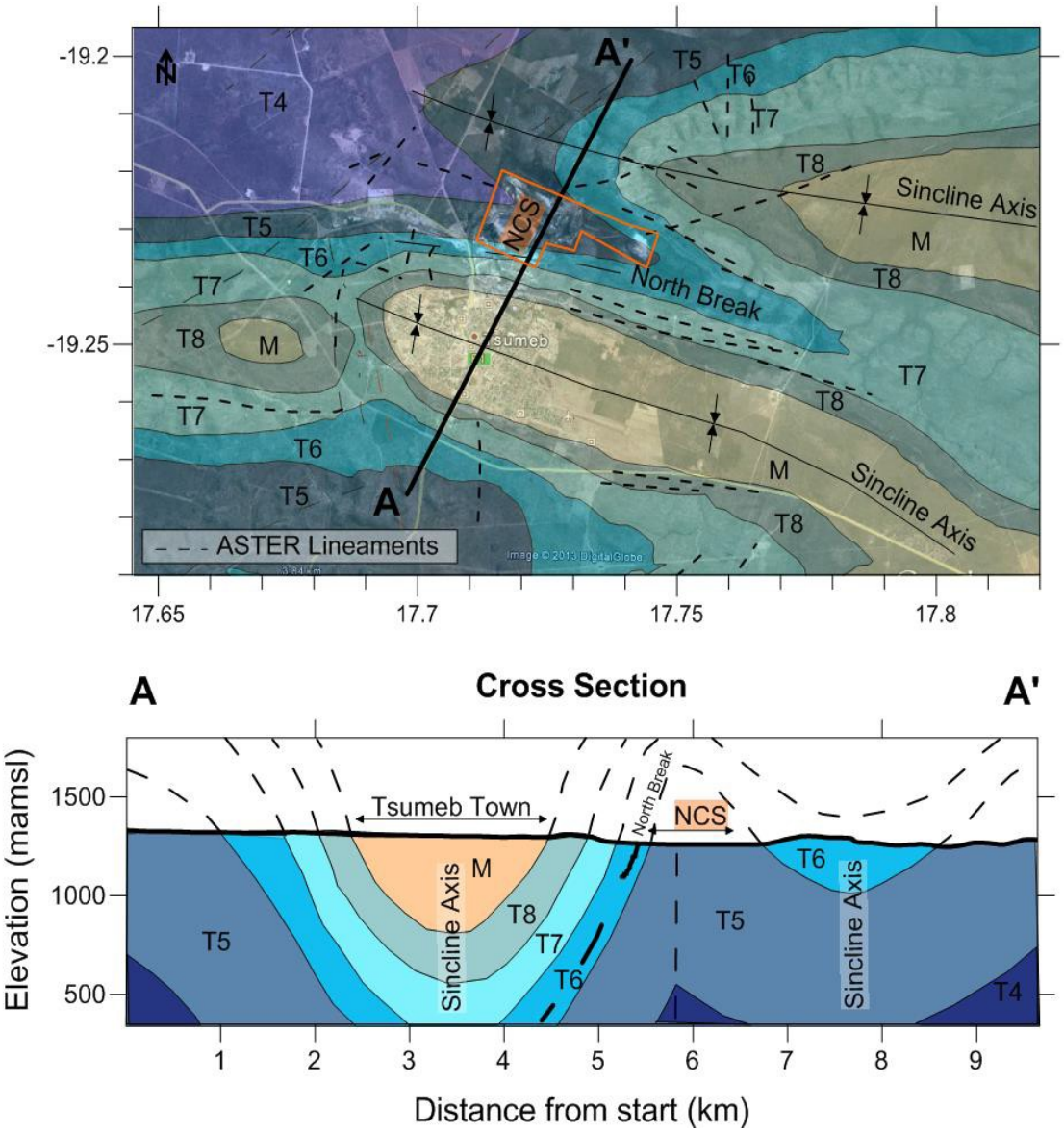


Figure 2-10 Local geology around the NCS site (Tsumeb Smelter), with SW-NE cross section through the site (Van Rooyen and Nel, 2013)

The detailed stratigraphy of the local geology around the Smelter area is presented in Table 2-2.

Table 2-2 Stratigraphic succession for the local geology around the NCS site or Tsumeb Smelter (Van Rooyen and Nel, 2013-edited)

Sequence	Group	Subgroup	Formation	Informal Lithozone	Lithology	Average thickness (m)
Damara	Mulden		Kombat and Tschudi	M	Kombat Formation: Slate,sub-arkose and pebbly sandstone near base	>700
					Tschudi Formation: feldsphatic sandstone, sub-greywacke;argillite and conglomerate interbeds in basal portion	
	Otavi	Tsumeb	Huttenberg	T8	Dolomite, bedded light to medium grey; oolitic chert and stromatolite layers near top	240
				T7	Dolomite, bedded dark grey; limestone, shale and chert interbeds	300
				T6	Dolomite, bedded dark grey; abundant chert; stromatolite interbeds in lower part	300
			Elandshoek	T5	Dolomite, bedded and massive light grey	1200
				T4	Dolomite, massive light grey	

2.3 Hydrogeology

2.3.1 Regional Hydrogeology

According to Golder Associates (2013), the Tsumeb Aquifers in the northern OML form an important regional groundwater resource for the water supply of the adjacent municipalities, irrigation and stock watering. The area has three (3) different aquifers that are distinguished as:

1) The Dolomite aquifer;
2) The Kalahari aquifer
3) Fractured dyke and fault systems

1) The Dolomite aquifer: The Dolomite Aquifer of the Tsumeb and Abenab Group has been described as low to medium permeable fractured rock. The carbonate rocks have little primary porosity but are locally enhanced due to intensive karstification at contact and tectonic shear zones. The transmissivity of the heterogeneous rocks locally vary between one to several hundred m^2/day.

An important variation in fractured hard rock aquifers are the carbonaceous rocks in which the fractures have been enlarged by the chemical solution of the rock in the water percolating through the aquifer system. These aquifers are called karstified aquifers and the aquifers in the Grootfontein-Tsumeb-Otavi Mountain Land are typical examples of the Dolomite aquifer group (Christelis and Struckmeier, 2011).

2) The Kalahari aquifer: The sediments consist of unconsolidated gravel and sands with intermittent layers of clay or calcrete. It is generally considered a porous aquifer although recent hydraulic tests indicate local compaction and fracturing. The Kalahari Aquifer increases in thickness towards the north, with transmissivity values of 5000 m^2/day having been measured in the Oshivelo Artesian Aquifer.

3). Fractured dykes and fault systems: In various geological provinces these systems are the least well known with respect to their hydraulic properties. The Tsumeb and Abenab mines are situated close to such structures and their presence and influence on the local hydrogeological system cannot be ignored. It

was concluded that Tsumeb dyke/fault system could be identified together with the Hüttenberg formation as the most permeable hydraulic units in the area. The clastic and metamorphic sediments of the Nossib and Mulden Group generally act as aquitards (Golder Associates, 2013). Within the Abenab (Otavi) Subgroup intermittent layers of quartzite, tillite, marble and shale have a low permeability. The Karoo deposits also have a low permeability and this separates the Kalahari aquifers from the dolomitic aquifer in the northern part of the study area. Table 2-3 shows different hydrogeological units in which each geological layer is associated with an aquifer type.

Table 2-3 Hydrogeological units (Van Rooyen and Nel, 2013-edited)

Sequence or Group (subgroup)	Formation	Hydrogeological Unit
Kalahari	Andoni	Unit 6: Frectured or porous aquifer
	Olukonda	
	Beiseb	
Karoo	Undifferentiated	Unit 5: Fractured aquitard
Mulden	Tschudi	Unit 4: Aquitard
Otavi (Tsumeb)	Huttenberg	Unit 3c: Fractured karstified aquifer
	Elandshoek	Unit 3b: Fractured aquifer
	Maieberg	Unit 3a: Aquitard
	Chuos	
Otavi (Abenab)	Auros	Unit 2: Fractured aquifer
	Gauss	
	Berg Aukas	
Nosib	Ghaub	Unit 1: Aquitard
	Nabis	
Basement Complex		Boundary: Aquiclude

2.3.2 Local Aquifer

The NCS site and the immediate surrounding area are underlain by a dolomitic massif consisting of interbedded layers of limestone, marble and shale. The dolomite aquifer dips underneath the Kalahari aquifer north of Tsumeb and have been described to be a low to medium permeable fractured aquifer (Van Rooyen and Nel, 2013).

Figure 2-11 shows a thick dolomite layer in a pit cutting located to the eastern part of the Tsumeb Smelter site area. The carbonate rocks have only little primary porosity and the permeability of the aquifers may be locally enhanced due to intense karstification at contact and tectonic shear zones.

Figure 2-11 Dolomite sequence located in the eastern part of the Smelter (Van Rooyen and Nel, 2013)

Indications are that structural controls may govern groundwater flow with potentially high yields at depth and groundwater is expected to move in e.g. fold axes, pressure relieve joints, faults or on contact zones of changes in lithology (Van Rooyen and Nel, 2013).

The aquifers underlying the NCS smelter can be divided into the following three (3) different components:

- Tsumeb fractured dolomite aquifer;
- Local karstification associate with bedding planes
- Fractured dyke and fault systems

2.3.3 Recharges and Discharges

The Otavi Group dolomite underlying the NCS site forms part of a regional aquifer system with primary recharge areas about 14 km to the South and discharge areas 60km to the North or in other words, the regional water level gradients are from South to North. The recharge in the Otavi Mountain Land is presumably larger than in the Kalahari due to the higher elevation and rainfall, and the exposure of the fractured or karstified dolomite. To date, very few to no investigations have focused on the quantification of the recharge in this particular area. Recharge rates of between 8 and 10% are expected based on experience on similar dolomitic systems in South Africa (Van Rooyen and Nel, 2013).

2.3.4 Pumping Tests

An aquifer testing was conducted on eight (8) of the existing boreholes at NCS; Slag 1, Slag 4, River, New Tailings 1, BH4 (also referred to BH5 sometimes), Waste Up 2, Maroela, Parking. The boreholes were pumped for periods between four (4) and eight (8) hours and then allowed to recover.

The tests were conducted during the week of 4-8 February 2013 by PJ Plumbing, an independent operator (contractor). Pumping rates were estimated based on geology and water level data obtained from the hydrocensus data. The aquifer response in all the boreholes were characterized with rapid drawdown, followed by constant rate, constant drawdown period until the end of the test. Recoveries in most of the boreholes were rapid (except Waste U2 which did not recover), typically lasting less than an hour (Van Rooyen and Nel, 2013).

Both the pumping phase and recovery phase of the tests were analyzed to obtain transmissivity. Observation boreholes were monitored during three (3) of the tests (Slag 4 with Slag 3 observation, Slag 1 with Slag 2 observation, BH4/BH5 with BH3 observation), providing the opportunity to interpret storativity values for the aquifer. Table 2-4 shows the summarized aquifer test results obtained from the selected boreholes at the Smelter in the year 2013.

Table 2-4 Aquifer test results for the selected NCS boreholes (Van Rooyen and Nel, 2013-edited)

Borehole ID	Pumping rate (l/s)	Drawdown (m)	Pumping Duration (hours)	Recovery Duration (hours)	Transmissivity Pumping Phase (m^2/d)	Transmissivity Recovery Phase (m^2/d)	Storativity (-)	Informal Lithozone
Parking	2.9	25	12.5	1	5	1	-	T6
Slag 4	9.5	30	8.0	1	51	3	-	T5
***Slag 3**	-	0.14	-	1.5	2200	-	0.0034	T5
Maroela	0.33	15	4	3.5	1.78	0.2	-	T6
Waste U2	0.17	16	1.8	3.5	0.58	0.35	-	T7
Slag 1	5.00	32	8.0	0.5	25	54		T5
****Slag 2**		1.6	-	-	54	-	0.00069	T5
New Tailings 1	1.83	7	4	0.5	17	17	-	T6
BH4	1.44	24	8.5	1	10	12	-	T5
*****BH3**		0.07	-	2	250	-	0.018	T5,Lineament
River	5.00	1.3	4	0.05	320	Very High	-	T5,Lineament

Note: *Slag 3 observed for Slag 4, **Slag 2 observed for Slag 1 and ***BH3 observed for BH4

As it can be seen in Table 2-4, Slag 1 and Slag 4 are the strongest boreholes in terms of drawdown, followed by Parking and BH4. Borehole Slag 3 has the highest transmissivity value of 2200 m^2/day. The high transmissivity in this borehole could be explained by it being located in a most transmissive hydrogeologic unit or this indicates the likelihood of one of the major fractured aquifers in Table 2-3. Small drawdown values were recorded for BH3 and Slag 3. However, the drawdown values for the latter boreholes are interesting as the drawdown suppose to be the difference between water level before and after

pumping, but according to the information in the table no pumping rate was recorded or carried out for these boreholes.

2.3.4.1 Groundwater Occurrence

From the monitoring survey conducted in 2012, groundwater was encountered in all the eight (8) site boreholes; Slag 1, Slag 4, River, New Tailings 1, BH4 (also referred to BH5 sometimes), Waste Up 2, Maroela and Parking. The boreholes information was recorded and is summarized in Table 2-5.

Table 2-5 Groundwater observation borehole information (Van Rooyen and Nel, 2013- edited)

Borehole ID	Elevation (ASTER GDEM) (mamsl)	Coordinates (WGS84 DD)		Static water level (mbgl)
		E	S	
Parking	1266	17.731078	19.22331	51.35
Slag 1	1254	17.72247	19.22021	46.41
Slag 4	1255	17.72260	19.22224	47.20
Maroela	1273	17.718460	19.234120	61.22
Waste Up 2	1326	17.720210	19.238200	84.46
Waste Up 1	1325	17.721542	19.238272	No data
Slag 3	1254	17.72216	19.22168	46.88
Slag 2	1256	17.72249	19.21964	46.61
***NT 1**	1283	17.740842	19.228436	70.72
***NT 2**	1277	17.742870	19.230040	66.92
BH5	1262	17.737919	19.229667	56.69
BH3	1262	17.73784	19.23038	56.91
River	1250	17.716780	19.216450	43.72
Calcine	1253	17.724544	19.222967	48.72
Tar Pit	1283	17.722853	19.234872	No data
Return Water	1253	17.719658	19.219500	46.29
Old Tailings	1261	17.715911	19.225114	51.05

Note: *NT1: New Tailings 1, ***NT2**: New Tailings 2

2.3.4.2 Groundwater Levels and Flow

According to Golder Associates (2013), the local groundwater flow pattern follows the regional northerly flow direction from the Otavi Mountain Land (OML) in the south, beneath Tsumeb towards the north. Groundwater flow is reported to occur primarily within the upper 150 m below surface although flow is reported to occur as deep as 900 mbgl (Van Rooyen and Nel, 2013). Karoo age dykes intersecting the entire dolomitic multi aquifer/aquitard system act as vertical conduits providing connections between otherwise vertically separated aquifer units.

A hydrocensus of boreholes undertaken by GCS in Van Rooyen and Nel (2013) across the DPMT site in late 2012 determined that groundwater levels ranged between 43.55 and 84.27 mbgl. The average groundwater level is deep at 54.88 mbgl. Groundwater levels on neighboring properties measured ranged between 19.07 and 41.81 mbgl (with an average value of 31.93 mbgl). Municipal water supply and monitoring boreholes again appear to have deeper water levels again, but only one of these boreholes was accessible to the GCS survey, Borehole 333373(A) with a water level of 75.65 mbgl.

GCS in Van Rooyen and Nel (2013) indicated that the groundwater levels on the DPMT site are deeper than on neighboring property, due to the higher topography. GCS also stated a ‘slightly southern dipping water table' even though regional groundwater flow directions are reportedly to the north. This may, therefore, be indicative of a localized, complex flow regime in the vicinity of the site, although overall groundwater elevations have not been taken into consideration.

The large differences in water table depths in relatively close proximity on the site and neighboring area may, however, be indicative of a flat regional groundwater table, created by highly transmissive aquifer conditions supported mainly by connected solution cracks and cavities along karst valleys, underlying a highly undulating surface topography. This is supported by a precursory examination of the GCS measured groundwater levels that indicate an approximate groundwater gradient of approximately 0.003 to the north, whereas

the topography drops at a gradient of approximately 0.009 over the same distance. This groundwater flow gradient and direction agrees with the value quoted by GKW Consulting (Unknown date) for the northern Elandshoek and Hüttenberg Formations. To the north of Tsumeb, groundwater flowing northward is assumed to mix with locally recharged groundwater of the Kalahari aquifer, which covers the Tsumeb aquifer. Here the topography and groundwater gradients assume similar flat values between 0.002 and 0.008 (Golder Associates, 2013).

The regional groundwater flow direction is from the Otavi Mountain Land, past Tsumeb, towards the north. The groundwater flow in the Tsumeb Dolomite Aquifers reportedly occurs within the upper 150 mbgl whereas groundwater flow at depths deeper than 900 mbgl is considered negligible. In the Tsumeb area, the Karoo dykes are considered vertical conduits which intersect the entire multi-aquifer/aquitard system. Towards the north of the regional aquifer the dyke and fault structures cut through the Karoo and locally connect the Kalahari aquifers with the Dolomite Aquifers (Van Rooyen and Nel, 2013).

Groundwater levels had probably been measured, but there was not enough data available on them, as it appeared that the Smelter's environmental department was more interested in the groundwater quality other than groundwater flow (The referential groundwater water levels referred to as "previous" reading before measuring the new levels in August 2014, was that from the 2013 report by Van Rooyen and Nel) and water levels from when the boreholes were drilled. During the author's short visit to the site in August 2014, groundwater levels for that month were measured and recorded as shown in Table 2-6 (as new static water level).

Table 2-6 Groundwater levels in monitoring boreholes (author, 2015)

Borehole ID	Coordinates (WGS84 DD)		Borehole Depth (m)	Previous static water level (mbgl)	New static water level (mbgl)
	East	South			
BH5	17.73791	19.22966	96	56.59	49.82
Return Water	17.71965	19.21950	110	45.00	46.56
River 1	17.71678	19.21645	100	43.00	44.44
Maroela	17.71846	19.23412	100	60.64	53.65
Waste U2	17,72021	19.23820	150	65.00	66.88
Waste U1	17.72154	19.23827	140	49.00	55.13
Parking	17.73107	19.22331	102	64.00	49.42
New Tailings 1	17,74084	19.22843	126	64.58	47.90
New Tailings 2	17,74287	19.23004	100	70.00	48.92
Calcine	17.72454	19.22296	110	54.69	49.00
Tar Pit	17.72285	19.23487	150	82.00	54.40
Old Tailings	17.71591	19.22511	110	57.00	45.00

Since groundwater level knowledge plays a great role in determining the general direction of groundwater flow throughout an area of interest, a 3D visualization, gridding, contouring and mapping software (Surfer v11) was used to construct a contour map for groundwater levels from the recent water level recordings in Table 2-6. Figure 2-12 shows a groundwater level contour map of the Smelter area.

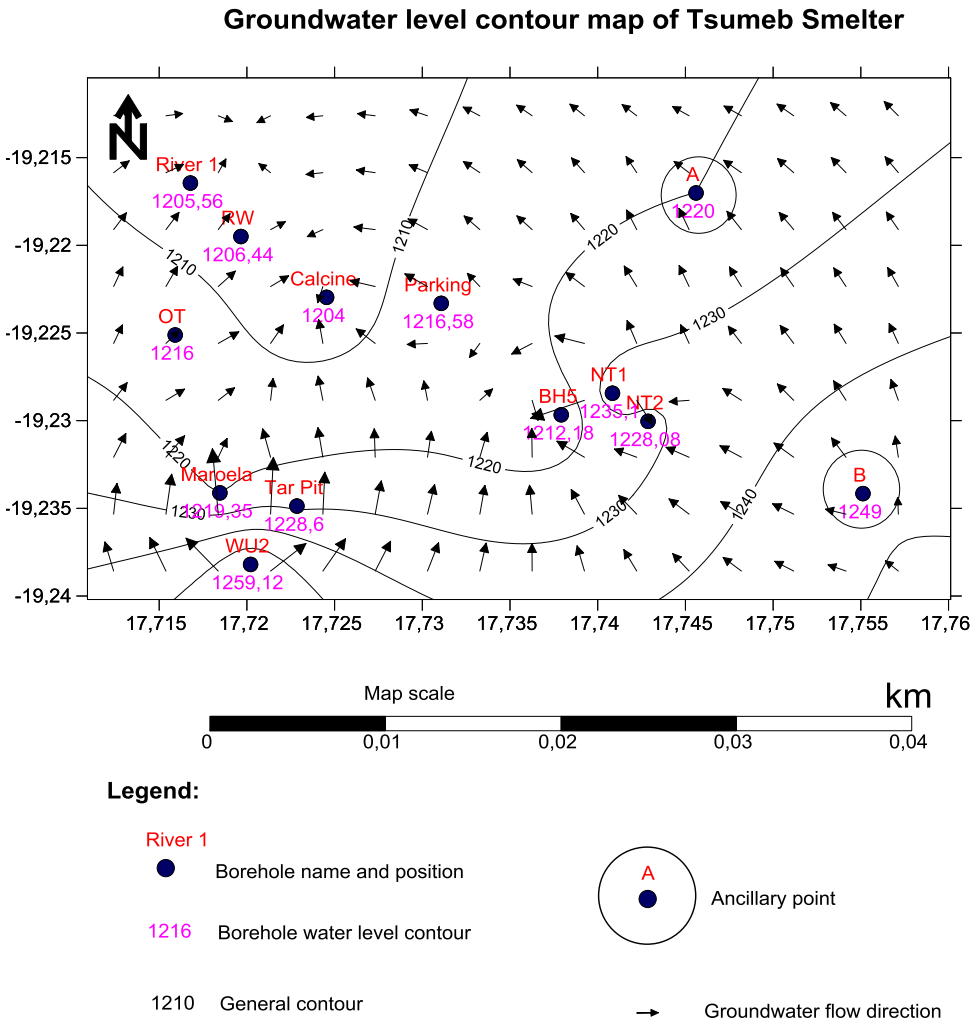


Figure 2-12 Groundwater level contour map of the Tsumeb Smelter (author, 2015)

From Figure 2-12, it can be seen that, the direction of groundwater flow across the Smelter as indicated by the arrows, is from the south to the north. Groundwater flows from areas of high hydraulic head (high water level elevation) to areas of low hydraulic head (low water level elevation) i.e. it flows down the hydraulic gradient.

The high water level elevation for New Tailings 1 (NT1) could be a result of perched aquifer in the tailings, which might have "manipulated" the actual water level in the boreholes.

The boreholes Waste Up1 and Waste Up2 are located very close to each other (few meters away from each other), for clear viewing of map details, only

Waste Up2 borehole was entered. Waste Up1 has a water level elevation of 1269.87 mamsl, whereas Waste Up2 has 1259.12 mamsl. The water level elevation difference of 10 mamsl between these two boreholes could only be attributed to geodetic survey error, since there are no regular hydraulic interferences like pumping that could have influenced water levels in the boreholes.

2.3.5 Hydraulic Properties

A detailed literature review was conducted by Bäumle in 2003 to collect hydraulic tests data for different units of the regional dolomitic aquifer (Van Rooyen and Nel, 2013). The summary of the aquifer hydraulic properties/parameters in terms of Transmissivity (T) and Storativity (S) values are shown in Table 2-7.

Table 2-7 Hydraulic properties of aquifer units (Van Rooyen and Nel, 2013-edited)

Stratigraphic Unit	T (m^2/day)	S(-)	Characterization
Basement Complex	n= 1 T<$5x10^{-3}$ m^2/d	n= 0	Aquiclude
Nosib	n= 3 T~ 3 m^2/d along fault zones T= 0.2 m^2/d undisturbed zones	n= 3 $1x10^{-3}$<S<$1.3x10^{-3}$	Aquitard
Abenab Subgroup	n= 5 14 m^2/d <T<466 m^2/d T= 0.08 m^2/d at depth > ~200m	n= 1 S= $6x10^{-4}$	Aquifer
Chuos	n= 1 T= 2.4 m^2/d	n= 1 S= $6x10^{-6}$	Aquitard
Maieberg	n= 4 87 m^2/d <T<123 m^2/d T= 0.4 m^2/d in the south	n= 2 3.10^{-5}<S<$1.6x10^{-4}$	Aquitard or Aquifer
Elandshoek	n= 8 15 m^2/d <T<1260 m^2/d Average T= 309 m^2/d	n= 1 S= 7.10^{-4}	Aquifer
Huttenberg	n= 8 121m^2/d<T<5565 m^2/d Average T= 1725 m^2/d T= 4 m^2/d at depth > ~300m	n= 5 4.10^{-4}<S< $1,6.10^{-2}$ S= $2.0.10^{-4}$ at depth > ~ 300m	Aquifer
Mulden	n= 1 T= 3.2 m^2/d	n= 1 S= $3x10^{-4}$	Aquitard
Karoo	n= 4 1.1 m^2/d <T<11 m^2/d	n= 4 $7x10^{-5}$<S< $3.0x10^{-3}$	Aquitard
Kalahari	n= 3 434 m^2/d <T<10367 m^2/d	n= 0	Aquifer

Taking a look at the values in Table 2-7 it can be seen that the Tsumeb aquifers, especially the Elandshoek and Hüttenberg with average transmissivity values of 309 m^2/day and 1725 m^2/day respectively, are potentially very transmissive formations on a regional scale due to their karstic nature, even though locally their low primary porosity may allow them to be considered low to medium permeable aquifers, as described by Van Rooyen and Nel (2013).

The hydraulic conductivity values of the aquifers were not provided and they could not be calculated, because there was no information on the thickness of the aquifers in the old site reports collected.

3 Monitoring of Groundwater Pollution

Groundwater monitoring plays a vital role in keeping track of the water status; quality and quantity, when a certain area is exposed to different anthropogenic activities that may pose great risks to groundwater, should these activities' resulting harmful substances come in contact with groundwater. Monitoring of groundwater requires installation of groundwater monitoring systems that enables collection of samples for analysis from the aquifer. These monitoring systems can be wells, boreholes, springs, ditches or any other object with an accessible water table.

According to the U.S. EPA (2014), the groundwater monitoring system consists of a series of wells placed upgradient and downgradient of the site. The samples from the upgradient wells show the background concentrations of constituents in the groundwater, while the downgradient wells show the extent of groundwater contamination. The required number of wells, spacing, and depth of wells is determined on a site-specific basis based on the aquifer thickness, groundwater flow rate and direction, and the other geologic and hydrogeologic characteristics of the site. All groundwater monitoring systems must be certified by a qualified groundwater scientist and must comply with the sampling and analytical procedures outlined in the regulation.

According to Šráček et al., (2002), monitoring of groundwater can be done for the following purposes:

- Monitoring of contamination plume movement from the source in the direction of groundwater flow,
- Monitoring the quality of groundwater flowing into a certain area (e.g. in the protection zone sources of drinking water),
- Preventive monitoring of groundwater quality around the place of production, transport, storage and handling of substances harmful to water (for example around chemical plants, along pipelines, fuel depots, landfills etc.).
- Monitoring the progress of the concentration of the contaminant in groundwater as a control for the efficiency of remediation,

- Qualitative and quantitative monitoring of groundwater abstracted water for drinking and other economic uses or purposes (for irrigation, reducing the groundwater level associated with construction or mining activities, etc.).

From the listed purposes of groundwater monitoring, the thesis focuses on the first one i.e. monitoring and prediction of contamination plume movement from the source in the direction of groundwater flow.

3.1 Groundwater Quality Monitoring History of the Smelter

According to Van and Rooyen (2013), in March 2006, possible metal contamination of the soil by dust outfall was suspected on the Smelter site and also in the surrounding area. Soil samples were collected and analyzed. The analysis showed high concentrations of arsenic (As), cadmium (Cd) copper (Cu) and lead (Pb). In more recent years, the sulfur dioxide (SO_2) emissions, arsenic levels and the amount of dust fall were monitored on a regular basis to minimize environmental impacts.

Surface water quality evaluations were performed on various sampling points in the site area. Sampling was primarily done during the spring period and served as a baseline description of the quality of surface water on site. Verification of the water quality confirmed good water quality and also contained insignificant amounts of arsenic (Van Rooyen and Nel, 2013).

Due to the fact that, the groundwater monitoring program was only started at the beginning of 2011 when DPMT took over ownership from previous owner, Weatherly Mining International in 2010, there is limited historical information (data) on groundwater monitoring. It was also said that most historic data related to both geological and hydrogeological data, that might have been available were lost during various ownership changes of the Smelter over the years. The recent previous owners of the site probably never carried out any groundwater monitoring.

3.2 Current Groundwater Quality Monitoring

Monitoring of groundwater on the Tsumeb Smelter has been carried out on a monthly basis by its assigned environmentalists.

GCS conducted a NCS site sampling and hydrocensus campaign in November 2012 on the boreholes shown in the water monitoring hydrocensus map in Figure 3-1. During the hydrocensus conducted in November 2012, a total of fifty (50) boreholes were visited. Twenty three (23) of the boreholes visited were located directly on the NCS site area, ten (10) boreholes were privately owned boreholes from the neighboring properties and the remaining seventeen (17) boreholes that were also visited are property of the local Municipality (Van Rooyen and Nel, 2013).

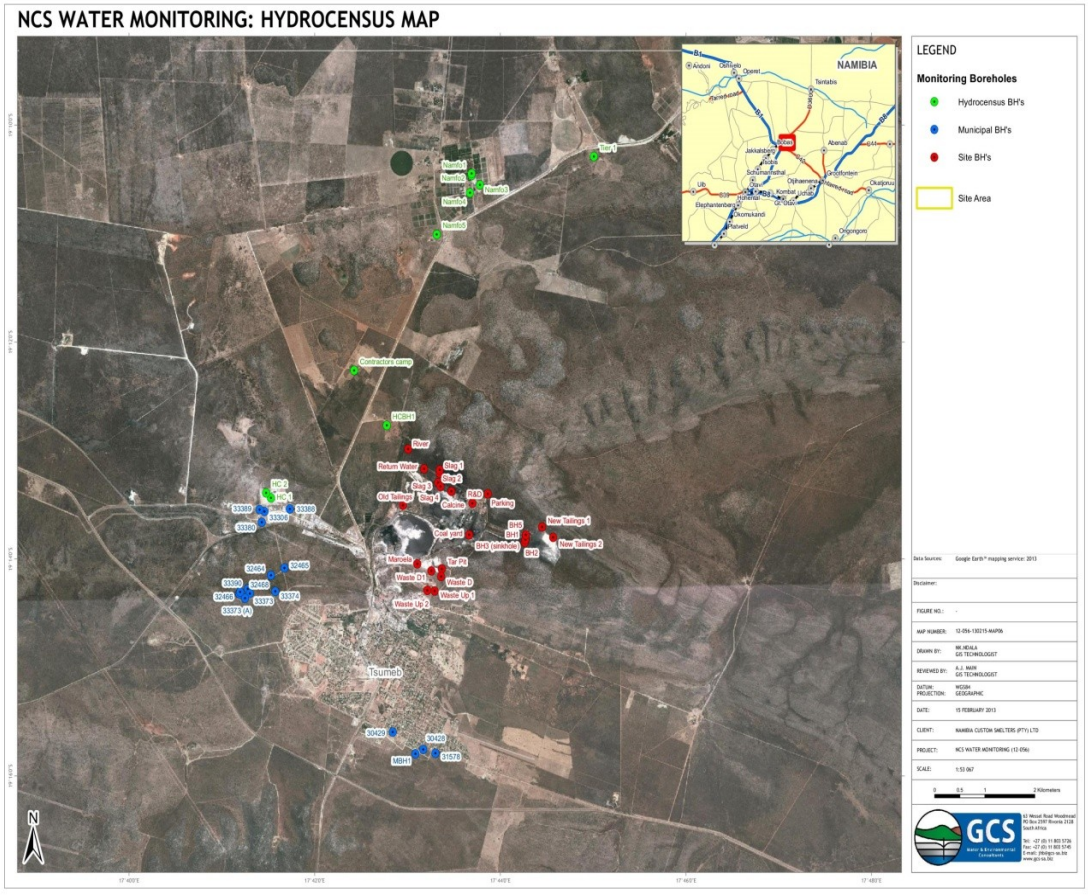


Figure 3-1 Boreholes visited by GCS for Hydrocensus in November 2012 (Van Rooyen and Nel, 2013)

Out of the twenty three (23) local NCS boreholes, only 12 of these have been equipped for monthly groundwater monitoring. The boreholes were named according to their position around the site, water monitoring role or according to a nearby significant object (e.g. River borehole). The boreholes names are; New Tailings 1, New Tailings 2, Borehole 5, Calcine, Maroela, Tar Pit, Waste Up 1, Waste Up 2, Old Tailings, Return Water 2, River 1 Water and Parking. The positions of the boreholes around the Smelter are shown in Figure 3-2.

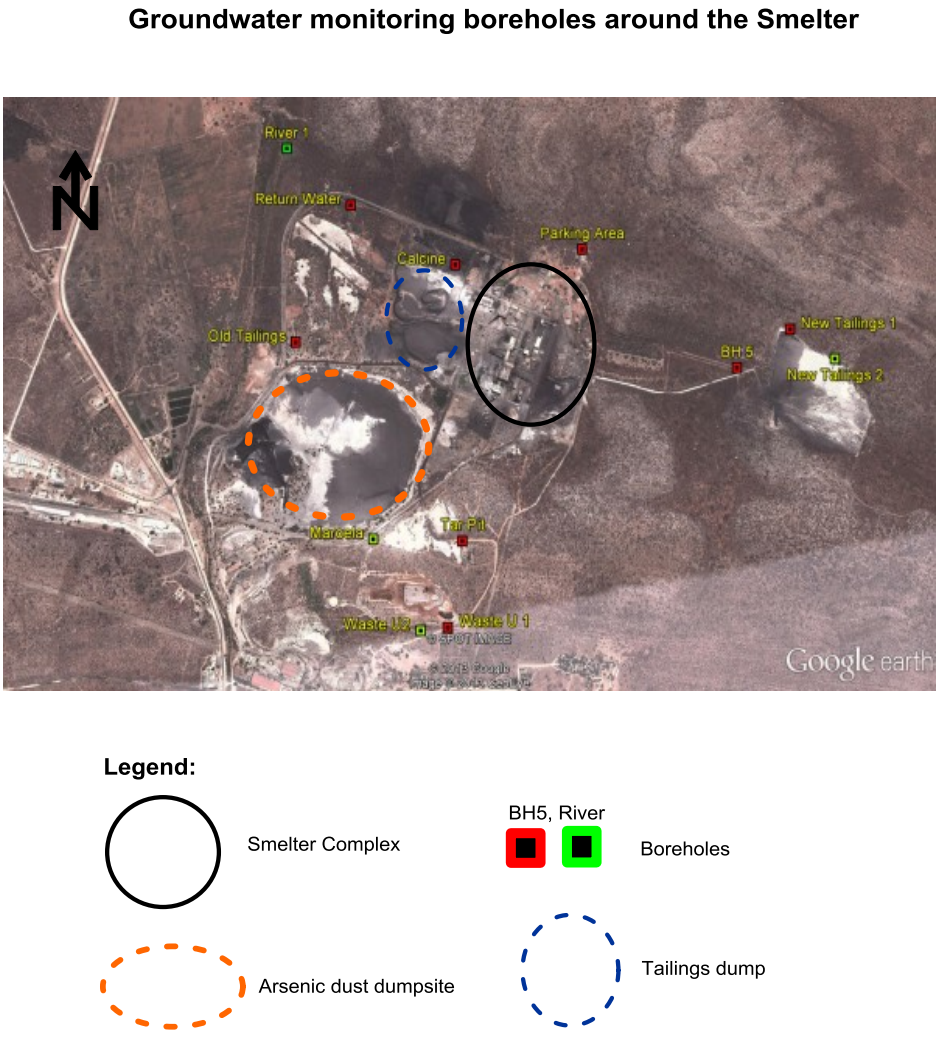


Figure 3-2 Location of NCS groundwater monitoring boreholes around the Tsumeb Smelter (author, 2015)

3.3 Groundwater Sampling and Preservation

During monthly monitoring at the site, water levels were measured with an electronic water level tape (equipped with a probe to detect the static water level) and recorded before purging. Borehole purging was done using a submersible pump and water samples were collected afterwards. Purging of boreholes before collecting water sample was necessary in order to remove stagnant water above the screen in the borehole. The stagnant water may have a different chemical composition than the water found below the screen due to its exposure to oxygen-rich atmosphere. For example, metals like iron that dissolved in groundwater may precipitate when exposed to the atmosphere for a while, and this affects water sampling and the analysis itself. During its November survey, GCS recommended purging times for the boreholes to be between 28 minutes and 2 hours. After the purging of each borehole, the collection of representative sample had to follow. Water samples for water quality analysis from each borehole have been collected after their respective (boreholes) purging time as per GCS recommendation. The purging durations are given Table 3-1.

Table 3-1 Borehole purging times as recommended by GCS (Van Rooyen and Nel, 2013)

Borehole ID	Purging time before sampling (hour, min)
New Tailings 1	1 hour 45 minutes
New Tailings 2	1 hour 00 minutes
BH5	1 hour 45 minutes
Calcine	50 minutes
Maroela	1 hour 15 minutes
Old Tailings	50 minutes
Parking	28 minutes
R&D	1 hour 15 minutes
Return Water	> 2 hours or discreet interval sampling
River 1	30 minutes
Tar Pit	> 2 hours or discreet interval sampling
Waste Up 1	1 hour 45 minutes
Waste Up 2	Pump needs to be installed deeper

After borehole purging, two (2) samples were collected from each borehole in one (1) liter sampling bottle. The samples need to be cautiously prepared and handled for later laboratory analysis. One sample was for major ion analysis

(acidified and unfiltered) and the second sample was for trace metal analysis, which is filtered and acidified to fix its chemistry and retain its original composition when delivered to the laboratory for analysis. The samples are acidified with nitric acid to obtain a pH value less than 2. According to Appelo and Postma (2005), acidification of samples stops most bacterial growth, blocks oxidation reactions, and prevents adsorption or precipitation of cations. However, the latter statement is not entirely true, because the acid does not literally stop the chemical reactions in the water, but rather slow them down, just enough time for the samples to be delivered to the laboratory for analysis.

Sample preservation was done at DPMT owned laboratory in the Smelter, but it is not yet accredited to analyze the samples. The purpose of filtering the samples is to remove bacteria and colloidal materials larger without contaminating the sample. Sample preservation at the Smelter was said (by GCS) to be done according to South Africa National Standards technique (SANS) 5667-3:2006. The samples were stored at 4°C in a dark clean container (out of direct sunlight) and transported to SGS laboratory in Swakopmund for chemical analyses within 7 days of being collected.

3.3.1 Groundwater Quality

Classification of water analyses serves as a tool for environmental authorities, water resource managers, drilling operators and practitioners to identify aquifers with good quality groundwater, and also useful for a first assessment of the relation between the aquifer mineralogy and groundwater composition. For example, groundwater from a limestone aquifer is likely to contain enhanced calcium and bicarbonate concentrations (Appelo and Postma, 2005). The knowledge of groundwater quality of an aquifer helps to enhance the decision-making of the use of the water by water resource management and other water related professionals.

The groundwater quality has been determined by collection of representative water samples from borehole. These groundwater samples were

taken to the laboratory for hydrogeochemical analysis. Although groundwater monitoring has been said to have started in 2011, the available data from that year was only for four months (January, February, March and July), and then seven months (March, June, July, August, September, October and November) in 2012 and then in the year 2014. Groundwater quality data for the year 2013 was not available.

Generally, there is no such thing as perfect chemical analysis of water samples done by the regular procedures. There will always be minor errors in the analysis. The purpose of the analysis is to make sure that, the sampling and the analyzing procedures of the water samples are well adjusted to get acceptable results. For best monitoring results and water quality analysis, it is important that sensitive components (parameters) like electrical conductivity (EC), pH, redox and temperature are to be measured in situ. Due to the fact that, the Tsumeb Smelter's environmental department has not been equipped with the required field tools to carry out these measurements in situ, water quality parameters have been just determined in the laboratory.

From the available water quality data for the twelve (12) monitoring boreholes, only two of the boreholes, Calcine and Return water were selected for the interest of this work, given their alarming arsenic concentrations. The results of the borehole water quality were compared to the Namibian Group A to Group D water quality standards and the World Health Organization (WHO) guidelines for drinking water.

3.3.2 Arsenic Concentration Levels

Arsenic, the contaminant of concern at the Smelter and an obvious interest for this thesis too, its groundwater concentration values were selected from the data provided by DPMT's (Smelter) environmental department and presented in Table 3-2. The concentration range levels are then illustrated on the site map in Figure 3-3.

Table 3-2 Borehole arsenic concentrations in mg/l (author, 2015)

	Borehole											
Date	**BH5**	**Calc**	**Maroela**	**NT1**	**NT2**	**OT**	**PRKG**	**RW**	**R1**	**TP**	**WU1**	**WU2**
Jan 2011	No data	No data	No data	No data	No data	0.05	No data	3.19	No data	0.08	No data	No data
Feb 2011	No data	No data	No data	No data	No data	0.05	No data	No data	No data	0.08	No data	No data
Mar 2011	0.03	2.4	No data	0.07	No data	0.05	No data	1.1	No data	0.08	0.08	No data
Jul 2011	0	0.61	No data	0	No data	0.11	0.05	2.9	No data	0.15	0.64	No data
Mar 2012	0.11	3.1	No data	0	No data	0.07	0.06	0.36	No data	0.08	No data	No data
Jun 2012	No data	11	No data	No data	No data	0.01	0.02	11	No data	0.01	No data	No data
Jul 2012	0	5.4	No data	No data	No data	0.01	0.03	7	No data	0.03	0.01	No data
Aug 2012	0	10	No data	No data	No data	0	0.04	14	No data	0.01	0.01	No data
Sep 2012	0	7.3	No data	0	No data	0	0.01	0.46	No data	0.01	0.02	No data
Oct 2012	0	8.2	0.01	0	0.01	0	0.01	8.10	0.01	0.02	0	0.02
Nov 2012	0.02	6.1	0.01	0	0.02	0	0.02	2.9	0.01	0.03	0.01	0.01
Jan 2014	0.012	6.1	0.096	0.003	0.023	0.004	0.015	4.1	0.01	0.03	0.004	0.007
Feb 2014	0.005	4.4	0.008	0.002	0.018	0.002	No data	3.4	0.008	0.017	0.003	0.01
Mar 2014	0.006	3.1	0.006	0.003	0.021	0.005	No data	*28	0.003	0.028	0.003	0.009
Apr 2014	0.003	3.1	0.001	0.0004	0.002	0.0004	No data	No data	0.011	0.028	0.011	0.002
May 2014	0.035	3.3	0.015	0.005	0.029	0.005	No data	No data	0.001	0.001	0.0004	0.006
Jun 2014	0.06	3.8	0,0009	0.009	0.009	0.0009	No data	8.6	0.014	0.033	0.009	0.0009
Jul 2014	0.089	2.5	0.006	0.003	0.017	0.004	0.01	7.6	0.009	0.014	0.004	0.006
Aug 2014	0.011	3.1	0.3	0.011	0.002	0.003	0.012	6.2	0.004	0.011	0.003	0.004
Sep 2014	0.013	2.6	0.3	0.003	0.02	0.005	0.017	7.1	0.00	0.012	0.005	0.007
Oct 2014	0.011	2.7	0.16	0.018	0.003	0.004	0.012	4.3	0.00	0.011	0.006	0.006
Nov 2014	0.002	2.5	0.012	0.002	0.007	0.002	0.03	0.82	0.00	1.9	0.002	0.002
Dec 2014	0.02	0.002	0.082	0.026	0.024	0.004	No data	4.3	0.01	0.01	0.004	0.009

*28 mg/l - error in analysis

Borehole abbreviations in Table 3-2:

- NT1, NT2-New Tailings 1, New Tailings 2
- Calc- Calcine
- Old Tailings- Old Tailings
- PRKG- Parking
- RW- Return Water
- TP- Tar Pit
- WU1- Waste Up 1 and WU2- Waste Up 2

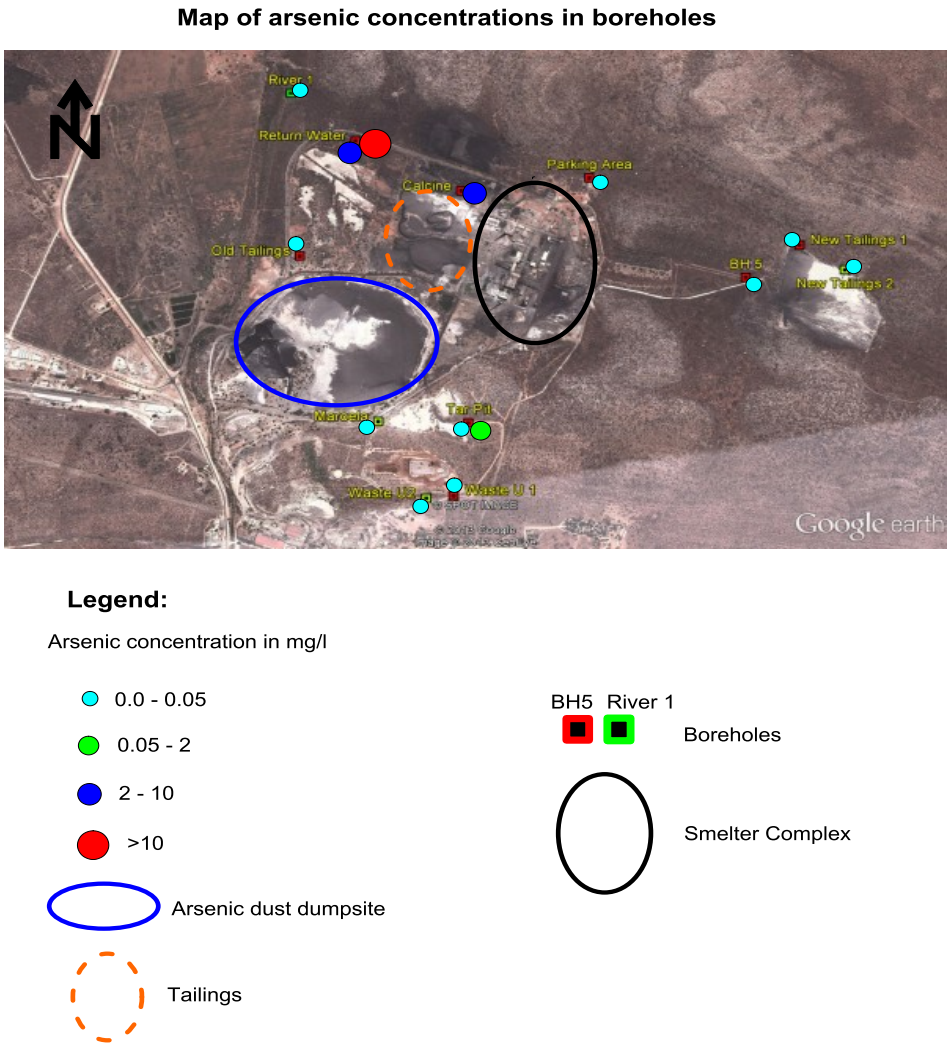


Figure 3-3 Arsenic concentrations in groundwater monitoring boreholes around the Smelter

According to Figure 3-3, the arsenic concentrations for both Calcine and Return Water ranging from 2 to 10 mg/l and concentrations greater than 10 mg/l shown by Return water (a probable analysis error), greatly exceed the WHO acceptable concentration of 0.01 mg/l and Namibian drinking water guidelines for both groups. The allowed arsenic concentration is 0.1 mg/l for group A, 0.3 mg/l for group B and 0.6 mg/l for group C and D. High concentrations of arsenic may pose a great health risk to the inhabitants, especially to farms in the northern side of the site.

A great concern is also on the concentrations in BH5 and Maroela boreholes, whose concentrations are only within the acceptable limit for Namibian group standard, but unacceptable for WHO standard for most months. Other boreholes also exceed the WHO limit in some months, but only by one order of magnitude. Table 3-3 shows the allowed arsenic concentration according to the Namibian and WHO drinking water guidelines.

Table 3-3 *Namibian and WHO drinking water arsenic limits (Walmsley and Tshipala, 2009-edited)*

		Namibian Drinking Water Guidelines				**WHO Drinking water Guidelines**
Constituent	**Unit**	Group A	Group B	Group C	Group D	
Arsenic	mg/l	0.1	0.3	0.6	0.6	0.01

The quality of groundwater should not always be evaluated according to drinking water standards, but it is equally important to do the evaluation based on environmental limits, that would be followed prior to the discharge of water into the environment. The general standards for waste/effluent water discharge into the environment should have a maximum allowable arsenic concentration level of 0.5 mg/l (Walmsley and Tshipala, 2009).

Apart from arsenic, chloride and sodium have also exceeded the environmental limits, as their measured concentrations are within ten and hundreds of milligrams per liter (mg/l) for all the boreholes. The maximum allowable levels for these components according to Walmsley and Tshipala (2009)

are 0.1 mg/l for chloride and sodium concentration should not be more than 90 mg/l.

4 Geochemical and Transport Processes, Prediction of Contaminant Plume Movement

The fate and mobility of arsenic are mainly controlled by five categories of processes in surface water and groundwater: (1) redox reactions; (2) adsorption and desorption; (3) competitive adsorption (ion exchange); (4) solid phase precipitation and dissolution; and (5) biological activity. These processes interact with each other and the mobility of arsenic may be controlled by multiple processes under a given set of conditions. Many factors, such as redox potential (Eh), pH or acidity, chemical composition of the system (e.g., redox pairs, competing anions, aquifer minerals, etc.), and reaction kinetics also play a role in these processes. Consequently, the occurrence, distribution, and mobility of arsenic are dependent on the interplay of these geochemical factors. Arsenic occurrence in groundwater world-wide shows significant spatial and temporal (to a less extent) variations, owing to the interplay among changes in the chemical composition and redox state of groundwater, microbiological activity, and adsorption and precipitation processes in the subsurface that establish and evolve within the overall hydrologic framework (Cheng et al., 2009).

Based on the arsenic geochemistry, there are three (3) major mechanisms controlling As mobility in groundwater, which have been reported by various workers. According to Sengupta (2014), these mechanisms are:

1) **Oxidation of pyrite**: Mobilization of As due to oxidation of arsenic-rich pyrite minerals associated with sediment and rock materials have been identified by many workers for different countries. Insoluble As-bearing minerals such as arsenopyrite (FeAsS) are rapidly oxidized when in contact with oxygen, releasing soluble As(III) and Fe(II). The oxidation of the As-bearing minerals is dependent on availability of oxygen. High oxygen in pyritiferrous system suffers by the excess pumping and water-table drawdown.

The rate of oxidation of pyrite is dependent on the redox potential (Eh) and pH. The release of Fe from pyrite oxidation can form Fe oxides that can immobilize As.

2) **Reductive Dissolution of Fe Oxyhydroxides:** Arsenic in Fe-oxyhydroxides is mobilized when the environment becomes anaerobic. There was a proposed reductive dissolution of Fe oxyhydroxides process for arsenic release. After that, many other studies conducted by numerous authors have also reported this mechanism. It was stated that there is a good correlation between As and HCO_3^- in groundwater is an indication of reduction. Other studies from Bengal basin reported that low Eh, O_2, NO_3^-, and SO_4^{2-}, and high Fe and Mn in groundwater are the indication of reducing conditions. The higher arsenic concentration in groundwater associated with lower Eh, NO_3, and SO_4^{2-}, and higher alkalinity, Fe, and PO_4 is the indication of reductive dissolution of Fe (hydr)oxides.
3) **Desorption of Fe-Oxydroxides:** Besides anaerobic conditions for releasing As from Fe oxyhydroxides, there is also effect of pH, particularly at pH > 8.5, which can cause mobilization of As from Fe-oxides.

4.1.1 Adsorption and desorption of arsenic species

Adsorption reactions between arsenic and mineral surfaces are generally considered the most important control on the concentration of dissolved arsenic in groundwater environments. Adsorption of arsenic is a complex function of the interrelationship between the properties of the solid surface, pH, the concentration of arsenic and competing ions, and arsenic speciation.

Arsenic species can adsorb on many soil colloids, including (hydr)oxides of iron, aluminum, and manganese, clay, calcium carbonate and organic matters. The adsorption capacity and behavior of these colloids are dependent on ever-changing factors, such as hydration, soil pH, and specific adsorption, changes in cation coordination, isomorphous substitution, and crystallinity (Cheng et al., 2009).

4.2 The Occurrence of Arsenic and its Behavior in the Environment

Arsenic (As) is a well-known toxic and carcinogenic metalloid that is found in a wide variety of chemical species throughout the environment and can be readily transformed and mobilized by microbes, changes in geochemical conditions, and other environmental processes (Bundschuh and Maity, 2013). Arsenic concentrations in groundwater vary greatly due to the heterogeneous distribution of source materials and subsequent geochemical controls on aqueous As mobility in aquifers. Flora (2015) indicated that, the presence of arsenic in water depends on pH, the redox condition of the solution, sorption, and exchange reactions. The causes of elevated arsenic concentrations in groundwater, including the complex interactions between water, geologic substrate and biological processes, are not yet completely understood. Dissolution and desorption of As from naturally occurring As-containing minerals, geothermal water, and mining activity appear to be the key contributors to high-As groundwater provinces within the United States (Peters and Burket, 2007).

Arsenic is present in the environment in both inorganic and methylated forms, though the inorganic species are considered to be the most prevalent in groundwater. Inorganic forms are common in As-containing minerals, adsorbed on amorphous Fe(III) oxyhydroxides, adsorbed on crystalline iron oxide phases, as surface precipitates on sulfides or pyrite, and as discrete nanoparticulate phases. Widespread occurrences of elevated As concentrations can be derived from oxidation of sulfide minerals, particularly trace-substituted pyrite and arsenopyrite (FeAsS), and also from desorption of As from mineral surfaces, or dissolution of the minerals with adsorbed As. In the case of As desorption from iron oxide minerals, redox conditions, pH, solid-to-solution ratios, specific surface area of minerals, and competing ions such as phosphate may affect As mobility and thus As concentrations in surrounding waters (Peters and Burket, 2007).

The most common arsenic species in both soil and groundwater are arsenite As(III) and arsenate As(V). Generally, oxidized arsenic in the neutral potential is present as $H_2AsO_4^-$ and $HAsO_4^{2-}$ as shown in Figure 4-1.

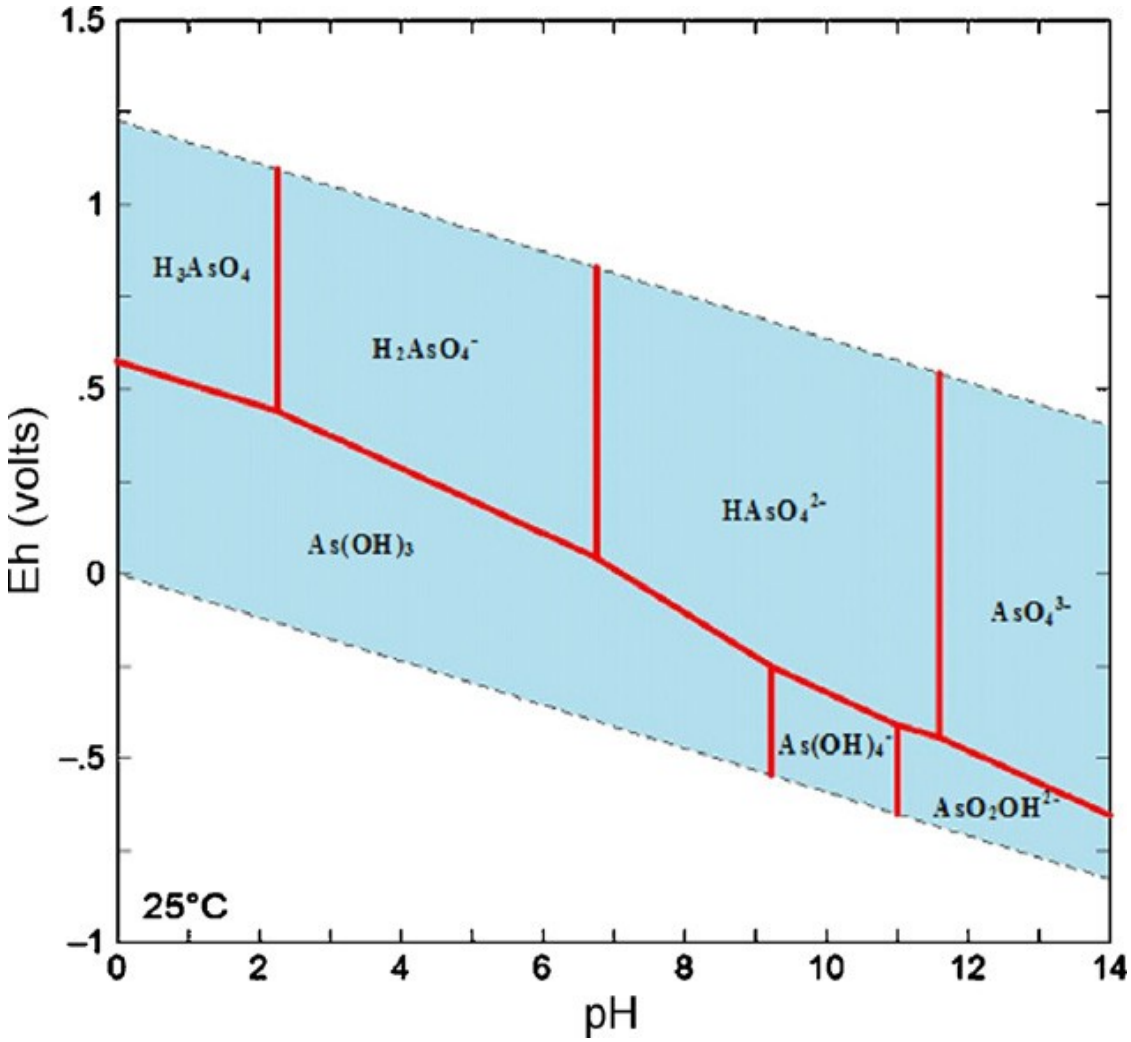


Figure 4-1 Eh-pH diagram for arsenic species (Cheng et al., 2009)

Arsenate generally predominates under oxidizing conditions, while arsenite predominates when conditions become sufficiently reducing. Redox reactions can control aqueous arsenic concentrations by their effects on arsenic speciation, and hence, arsenic adsorption and desorption.

Reduced arsenic in a wide pH range is present as H_3AsO_3. The only mineral As(V), of which its precipitation can control the concentration of arsenic in the oxidation environment, is scorodite ($FeAsO_4.2H_2O$). This mineral, however, is only stable at a pH of about 4.5 and precipitation occurs only at very high concentrations of As(V) and Fe(III). Less soluble $Fe(OH)_3$ has a much greater effect on reducing the concentration of arsenic in water. Both forms of arsenic are

adsorbed on the $Fe(OH)_3$, but the As(V) has a greater affinity for adsorption than As(III) (Šráček et al., 2002).

Adsorption of As(V) decreases with increasing pH (maximum at around pH of 4.0), because As(V) is present as an anion. Conversely, As(III) present in neutral form has adsorption maximum at neutral pH. Another problem is the instability of $Fe(OH)_3$ and the releasing of the adsorbed arsenic due to the drop in Eh and pH. Usually with senescence, amorphous $Fe(OH)_3$ leads to its crystallization and transformation into goethite thereby leads to the reduction of the surface available for adsorption and desorption of arsenic at the same time. Another factor which may cause desorption of arsenic, is its displacement from the adsorption sites by other strongly adsorbed anions such as phosphates or sulfates, whose concentration in the water are also usually higher than the concentration of arsenic (Šráček et al., 2002).

4.2.1 Sources of Arsenic

4.2.1.1 Anthropogenic Sources

Sources of As that arise from human activities include mining and processing of ores and manufacturing using As-bearing sulfides. Smelters in numerous countries worldwide have processed metal ores (mainly copper, but also zinc, gold, and tin) that contain As (Barringer and Reilly, 2013). The disposals of mining and ore processing wastes have caused arsenic contamination of groundwater in many places in the whole, as arsenic is released from tailings into groundwater through leaching. Figure 4-2 shows a general mine tailings impoundment-aquifer interaction and associated geochemical pH-buffering regions.

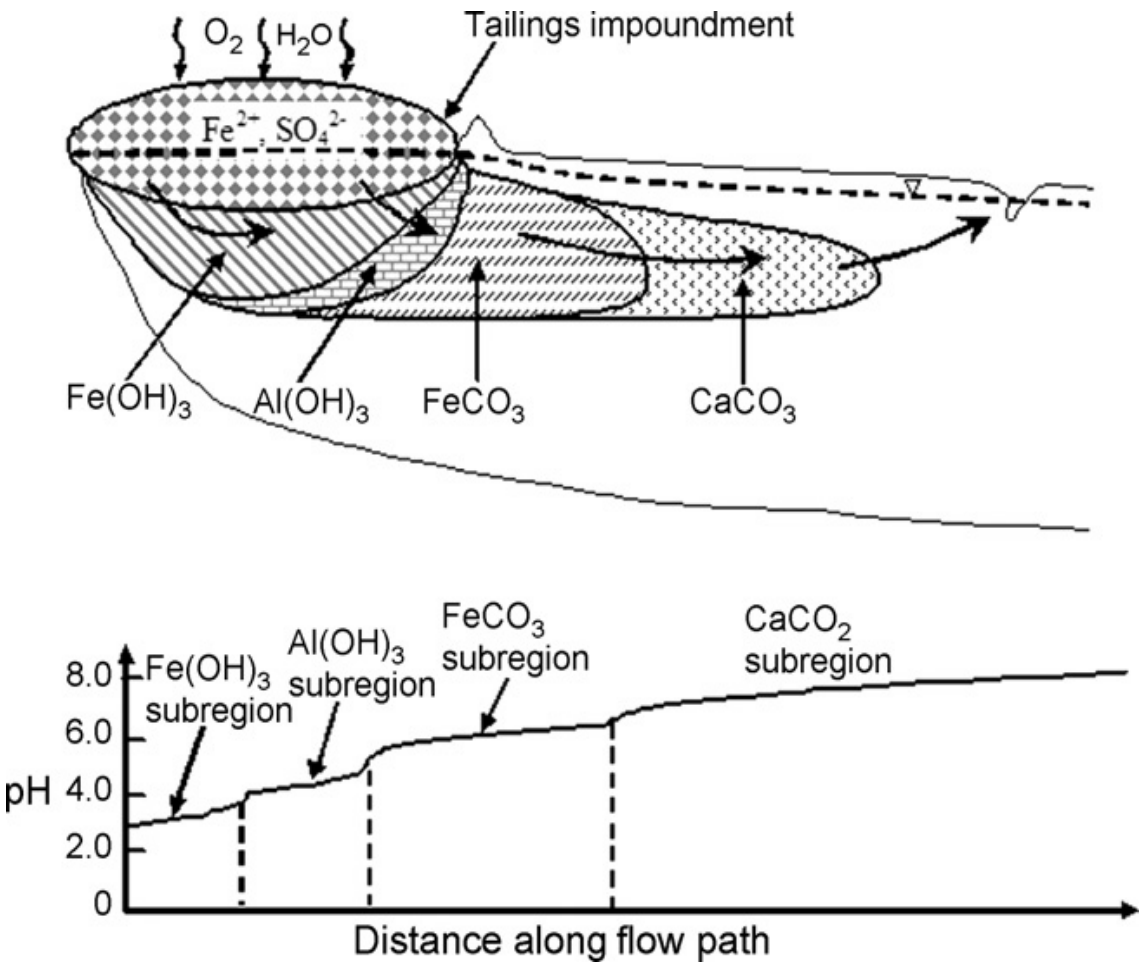


Figure 4-2 Schematic diagram of mine tailings impoundment and underlying aquifer, and the associated geochemical pH-buffering regions (Cheng et al., 2009)

Arsenic compounds have been used in the manufacture of numerous products. Arsenic has been used in glass production and by the wood-preservation industry. The use of inorganic arsenical pesticides has waned in recent years owing to bans in the 1980s and 90s, but, in the past, manufacture and use of arsenical pesticides were main contributors of As to the environment. Anthropogenic sources of As can affect the quality of surface water through groundwater discharge and runoff. In the case of pesticides, the effect can be through direct applications to water bodies for control of nuisance vegetation.

Although groundwater contamination does exist at various sites affected by agricultural, industrial or military releases, contamination introduced at the land surface does not always move to groundwater. Owing to the affinity of As for soil

constituents such as metal oxides and hydroxides (mainly iron (Fe), aluminum (Al), and manganese (Mn)) and clays, As can be attenuated in the intervening soils by sorption to iron hydroxides or clays, or by precipitation reactions, such as formation of As- or Fe-sulfides in anoxic soils (Barringer and Reilly, 2013).

4.2.1.2 Geologic Sources

According to Barringer and Reilly (2013), for most known a really extensive instances of As contamination of groundwater, the sources of As have been shown to be geogenic. Most primary As minerals are sulfides, of which arsenopyrite is the most common. Secondary minerals tend to be less common arsenates and oxides. Arsenic in crustal rocks also has an affinity for, and is associated with, pyrite or Fe hydroxides and oxides for which chemical formulas are FeS_2, FeOOH, Fe_2O_3, and Fe_3O_4, respectively.

The second geologic sources of arsenic are sedimentary and meta-sedimentary bedrocks. Coal is one of the sedimentary rocks that contain arsenic. Coal are known to contain the mineral pyrite which has a high As content, whereas in lower As coals, the As tends to be associated with the organic material (Barringer and Reilly, 2013).

The third geologic sources of arsenic are geothermal activity, volcanic and plutonic rocks, and mineralized zones. Arsenic is released from the host rocks of the geothermal reservoir. Significant quantities of As are leached from non-mineralized andesite during hot water–rock leaching experiments with As concentrations up to1300 µg/kg in the leachate. The high residence time of the fluids in the reservoir, high temperature and pressure, and the reducing conditions (prevalence of As(III) and thioarsenites), which have higher mobility than As(V)and thioarsenates, together with under saturation of most reservoir fluids regarding to arsenopyrite and other As minerals favor dissolution of As (Bundschuh and Maity, 2013).

High As concentrations in geothermal waters have been described over a century ago and common concentrations are in the range of thousands to tens of thousands of mg/l. Naturally occurring As in groundwater associated with

terrestrial geothermal activity is recognized to be significant and has been identified in many areas of the world including Alaska, western USA, Mexico, Central America, Northern Chile, Kamchatka, Japan, Taiwan, Philippines, Indonesia, Papua New Guinea, New Zealand, Iceland and France (Bundschuh and Maity, 2013).

4.3 Processing of Annual Hydrogeochemical Data

4.3.1 Groundwater Chemistry Analysis

Data on hydrogeochemistry was collected from the twelve (12) boreholes between January 2011 and November 2012 and then from January to December 2014. No data was available for the whole year of 2013. For a reliable evaluation, prediction and development of a contaminant, it is important to have monthly data throughout the year. Regular monitoring of groundwater quality over the years would help to evaluate the development of contamination with time.

The water chemistry analyses for Calcine and Return Water boreholes were chosen for their high arsenic concentration. The groundwater chemistry for major cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}), anions (SO_4^{2-}, Cl^{-}, HCO_3^{-}, NO_3^{-}, NO_2^{-} and PO_4^{3-}), heavy metals (As, Fe) and trace metals (Zn, Cu, Mn, Pb, Cr and Mo) were selected and graphed to show the development of the groundwater chemistry with time.

For a brief insight into the water chemistry of these two boreholes, their chemical analysis results for some cations and anions constituents in December 2014 were selected. The rest of the constituents were ignored due to their relatively small and undefined concentration values, which made it hard for them to be included in the graphs. The water chemistry summary is presented in Table 4-1.

Table 4-1 Selected groundwater chemistry for Calcine and Return Water in December 2014 (author, 2015)

Constituents	Units	Calcines	Return Water
pH at 25°C	-	7.3	7.3
Electrical Conductivity EC	mS/m	252	200
Total Dissolved Solids TDS at 105°C	mg/l	1700	1300
Calcium Ca^{2+}	mg/l	241	175
Magnesium Mg^{2+}	mg/l	No data	No data
Sodium Na^{+}	mg/l	176	158
Potassium K^{+}	mg/l	14	12
Sulphate SO_4^{2-}	mg/l	1020	681
Bicarbonate HCO_3^{-}	mg/l	289	392
Nitrate NO_3^{-}	mg/l	15	<0.1
Chloride Cl^{-}	mg/l	80	121
Nitrite NO_2^{-}	mg/l	0.07	0.08
Phosphate PO_4^{3-}	mg/l	0.18	1.4
Arsenic As	mg/l	3.8	4.3
Iron Fe	mg/l	0.97	0.68
Zinc Zn	mg/l	0.07	0.08
Copper Cu	mg/l	0.005	0.006
Manganese Mn	mg/l	<0.002	0.65
Lead Pb	mg/l	0.001	0.001
Molybdenum Mo	mg/l	1.1	0.46

From Table 4-1, the water from Calcine and Return Water borehole shows the same pH value of 7.3. This similarity (which is the case for more than half of the other 10 boreholes with a pH value range from 6 to 8.8, might be because the Tsumeb Smelter is geologically located in the carbonate rich rock area (dolomite and limestone), which is expected to show the neutral to alkaline behavior. The high concentrations of constituent concentration in groundwater are explained under appendices explanations from page 60.

The groundwater chemistry for the selected components from 2011 to 2014 were graphed and presented in appendices 1 to 12 at the end of the thesis. Calcine borehole water chemistry is illustrated by graphs in appendix 1 to 6 and Return Water from appendix 7 to 12. The missing data for most months in 2011, 2012 and the whole of 2013 inflicts the splitting of trends in the graphs. Explanations to the appendices (graphs) are as follow:

- **Appendix 1: Major cations (calcium, magnesium, sodium and potassium)**

The high calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations are expected in dolomitic groundwater, because these two are major constituents of dolomite which form the local rocks units; dolomite and limestone, so their high concentrations in all the water samples are not surprising. Calcium is usually released into the water from carbonate rock dissolution and a certain amount of calcium could have also been originated as lime in agricultural fertilizers from the nearby farms.

In 2014, for some unexplained reasons, magnesium is missing in all the water chemistry analyses or it was perhaps not detected in the samples. Magnesium is one of the major ions in water and also one of the primary elements contained in dolomitic rocks (main geologic unit around the Smelter), so its absence in the sample analyses is very strange.

Sodium (Na^{+}) and Potassium (K^{+}) are some of the major ions expected to be found in groundwater. Lower concentrations of potassium in the borehole are probably due its excessive uptake by plants or natural exchange processes that remove it from groundwater. The potassium in the water is released from rock-water interaction.

- **Appendix 2: Major anions I (sulphate and bicarbonate)**

Sulphate (SO_4^{2-}) high concentrations, apart from it being one of the major water anions, it is likely to present in such amount, due to the natural composition of the ores, pyrite (FeS_2) and arsenopyrite (FeAsS) that are processed at the Smelter. The mineral wastes end up on the tailings, exposed to weathering and where they react with oxygen, resulting into sulphate formation. The sulphate is then leached into groundwater through rainwater infiltration into the ground. With Calcine being located very close to the some of the tailings pile, this could also explain the high concentration of sulphate above that of any other borehole.

Apart from naturally occurring sulphate and sulphate-bearing ore, the application of agricultural fertilizers in farms in the vicinity of the Smelter might have contributed a certain amount to the elevated sulphate levels.

Bicarbonate (HCO_3^-) high concentration levels are due to the mineral composition of the site rock unit, since Tsumeb Smelter is geologically located in a carbonate rich rock units (dolomite and limestone). This is a principal anion in groundwater and given the nature of the study area its concentration values are rational.

- **Appendix 3: Major anions II (nitrate and chloride)**

Nitrate (NO_3^-) is a common groundwater contaminant which occurs naturally or can be introduced to it by man-made sources like commercial fertilizers from nearby farms or by chemicals used for smelting processes. Nitrate levels in groundwater vary considerably both spatially and seasonally which explains it high concentration during rainy season. Some of the highest nitrate concentration levels in Calcine were recorded in January, April and May 2014, when rain usually maximizes the rate of leaching of fertilizers or nitrate containing chemicals in the soil with concentrations increasing in July.

Chloride (Cl^-) is one of the principal anions in groundwater and its high concentration values are rational. The split in chloride graph trend in May 2014 is caused by an absence of data (removed), because a very small value of 0.05 mg/l was recorded that month and this was considered a measurement error (outlier), thus its exclusion from the data set.

- **Appendix 4: Other anions (nitrite and phosphate)**

Nitrite (NO_2^-) occurs naturally in groundwater as product of reduction reactions of nitrate to form the nitrite ion. This usually happens deep within the borehole, where the level of the favorable electron acceptor, oxygen is depleted (anoxic conditions). The highest data point of 15 mg/l for nitrite concentration in December 2014 indicates a measurement (analysis) error and was excluded from the graph.

Phosphate (orthophosphate, PO_4^{3-}) occurs naturally as a free ion or chemically attached to sediments and soils, or as mineralized compounds in soil, rocks, and sediments. Phosphate can be attributed to anthropogenic sources like untreated sewage from Smelter or agricultural fertilizers from nearby farms. The low concentration levels indicate that the sewage and waste waters from Smelter activities are either well-treated before it is released into the environment or phosphate is used at a minimum level in the farms.

- **Appendix 5: Heavy metals (arsenic and iron)**

Total arsenic (As), apart from it being originally natural sediment-water interactions, the high concentrations of arsenic in the boreholes could also be explained by the flushing out of a significant amount of arsenic from tailings dumps during rainy season between October and March. The main contributor to the elevated concentration is the oxidative dissolution of arsenic-bearing minerals when interacting with water and also the weathering of these minerals on the tailing leading to the release of arsenic. Another reason could be that, the borehole is located in the hydrologic downgradient close to the tailings, that the arsenic from the tailings is carried directly into the borehole with groundwater flow. Long pumping/purging duration could also be another explanation for high arsenic concentration in this borehole, as this leads to excessive migration of arsenic from the aquifer into the borehole.

The green trend titled "As Enviro limit" marks the maximum allowable arsenic concentration (0.5 mg/l) in the waste water that can be discharged into the environment.

Total iron (Fe) concentrations, observed in the boreholes, have been attributed to its presence in mineral ores, pyrite and arsenopyrite and it ended up on the tailings dump with other ore processing wastes.

- **Appendix 6: Trace metals (zinc, manganese, copper, lead, molybdenum)**

The high concentration of Zinc (Zn) in June 2012 is an analysis error, because it is greatly higher than other concentration values in other months. The

other metal with concerning concentrations is molybdenum (Mo). Molybdenum is naturally present at low concentrations levels in the environment and its high concentrations in groundwater can be explained by molybdenum-containing waste materials produced from ore processing and deposited at the tailing impoundment which is later washed off by rainwater into groundwater. The highest concentration of 5.5 mg/l for molybdenum in June 2014 reflects a measurement error and it was excluded from the graphed data.

Other trace metals like zinc, manganese and lead occur in low concentration. Copper being the targeted metal from the ores, most of it, is "captured" as blister copper during smelting and very little is deposited as waste material on tailings, hence low concentrations in groundwater.

- **Appendix 7: Major cations (calcium, magnesium, sodium and potassium)**

There was no data recorded for Return Water in April and May and this could be that for some reasons, there was no monitoring done on this borehole in these months. However, similar explanations on constituent concentrations in other months are expected to be the same as that of Calcine borehole graph in appendix 1.

- **Appendix 8: Major anions I (sulphate and bicarbonate)**

Same explanation as that was given for Calcine borehole graph in appendix 2.

- **Appendix 9: Major anions II (nitrate and chloride)**

As explained in appendix 3.

- **Appendix 10: Other anions (nitrite and phosphate)**

The reasons for these anions concentrations were given in appendix 4.

- **Appendix 11: Heavy metals (arsenic and iron)**

Elevated arsenic concentration in March 2014 is attributed to measurement error.

- **Appendix 12: Trace metals (zinc, manganese, copper, lead, molybdenum)**

An elevated zinc concentration in August 2014 is a result of analysis error. Manganese occurs naturally from the weathering of minerals and rocks that contain it and this explains the low concentrations in groundwater. Manganese that migrates to local groundwater could also been originated from Smelter processing activities, sewage, and leaching from tailings.

4.4 Methodology

4.4.1 Hydrogeochemical Modeling

The geochemical model PHREEQC for Windows was used to simulate reactions in order to predict the behavior and movement of arsenic. Geochemical modeling was carried out based on collected groundwater samples from the two (2) selected boreholes, Calcine and Return Water. Since arsenic could not be recognized by PHREEQC, aluminum (Al) was used to represent it during calculations. There was no data on the temperatures of the water measured directly in the boreholes, so the laboratory sample analysis temperature of 25°C was used for modeling. The sample pH values used in the calculations were also just determined in the laboratory.

4.4.2 Geochemical modeling Results

The calculations performed in PHREEQC model did not make sense, as it would have been expected in reality, if the above mentioned parameters were measured in the field and this led to wrong and unrealistic results.

4.5 Prediction of Contaminant Plume Movement

PHREEQC was supposed to be used for contaminant plume movement prediction, but this was impossible, because the input parameters; pH, temperature and Eh were not measured directly in situ. The laboratory temperature of 25°C was used for all the water samples, but the waters have

different temperatures in each borehole, and their temperature value would have been smaller than that of the laboratory set value. Like water temperature, oxidation-reduction (redox) potential (Eh) is also best measured in the field under controlled conditions, as exposure to the atmosphere can quickly invalidate the measured value.

Due to missing data on field-measured pH, Eh and water temperature, which resulted in wrong calculations performed by PHREEQC, the prediction of arsenic development was done based on the graph trends in appendices at the end of this work. The graph trends show that the development of water chemistry will remain the same for some time, which means there will not be a decrease nor increase in arsenic concentrations. During rainy season, some mobile components easily get into groundwater, while in dry season, the component concentrations increase in the water due to high evaporation. Prediction is expected to be the same in future, provided that the conditions remain the same.

According to a recent geophysical survey done at the Smelter, electrical methods (resistivity imaging) were successful to identify that the contaminant plume migration is from the Smelter's tailings dams (Nel, 2014). The concentrations of arsenic in Calcine and Return Water boreholes on the side of tailings dam reflect this reality. The direction of the contaminant plume movement is in the same direction as groundwater flow, from the south to the north of the Smelter.

The geophysical survey was assumed to be an ongoing one, because the report literature was still to be completed.

5 Discussion

Based on the geochemical modeling and chemical data, the environment is oxidizing, due to the transport of samples to the laboratory. The chemical analyses were carried out at SGS laboratory in Swakopmund, which is about 500 km from the Tsumeb Smelter. The time that elapsed between sample collection and analyses was too long, that it caused significant changes in pH, Eh and temperature. These changes would cause a big discrepancy between parameters measured in the field and parameters determined in the laboratory.

Given the borehole depths ranging from 90 to 150 m, reducing conditions are expected to take place in these boreholes. This is because when the water from the surface infiltrates into the ground, it carries dissolved oxygen with it, and as the water continues to flow downward, it loses contact with the atmosphere. The dissolved oxygen slowly gets consumed up and reducing conditions become stronger as the depth increases.

The movement of arsenic in groundwater is mostly controlled by sorption (adsorption and desorption), reduction-oxidation and precipitation-dissolution reactions. The adhesion of dissolved arsenic on mineral surfaces or solid materials within the aquifer inhibits its mobility. Desorption, the opposite process of arsenic adhesion (adsorption) on surfaces, occurring predominantly in oxidizing environments, removes the arsenic from these surfaces and releases it into the surrounding groundwater. Desorption of arsenic occurs when water pH value decreases (acidic) or when competing ions like phosphate reduce arsenic adsorption on sorption site (mineral surfaces), which makes it mobile again and free for the next available adsorption surface.

6 Recommendations

To improve the knowledge base and minimize further transport of contaminants into groundwater and improve the quality of groundwater, the following measures need to be taken:

- Carrying away tailings and designing a landfill that will capture arsenic leachate and prevent from infiltrating into groundwater (rock environment) through its base and sides.
- Isolation of tailings from groundwater by using liners (plastic or textile liners).
- Mothballing the arsenic produced during smelting to prevent it from spreading into the environment and to reduce its concentration levels in groundwater.
- Improving the quality of sampling methods in the field.
- Field parameters like pH, Eh and water temperature should be measured directly in the boreholes.
- Time between sample collection and their analyses should be minimal.
- The distance between sample collection site and the laboratory carrying out the analyses is alarming. An immediate solution is required.
- Measuring of groundwater levels and keeping record of the measurements helps future groundwater quantity evaluation and studies, not only groundwater quality, as groundwater flow direction controls pollution transport mechanisms like advection.
- More boreholes should be drilled downgradient of the Smelter. The purpose is to have enough boreholes in this direction to have a better understanding of the changes in groundwater levels with time. More boreholes drilled in this direction and adjacent to the source zones would help to determine contaminant plume length (how far the "face" of the contaminant plume has reached or has not reached yet) as well as its width.

7 Conclusions

The objective of the thesis was to predict the movement of the contaminant plume from the source into the direction of groundwater flow from Tsumeb Smelter in Namibia using a geochemical model PHREEQC. The main focus was placed on arsenic as the major contaminant of concern and other possible minor contaminants on site.

The objective was not properly accomplished, due to insufficient data. The input water parameters like pH, Eh and temperature used for geochemical calculation were laboratory determined. The calculations were performed with the same temperature, which is not correct, as different waters have different temperatures in the boreholes. The model requires field measured data, which was not available and this led to wrong results.

The monitoring of groundwater quality has been done for four years at the time this work was written. This however, is not a long time to make long-term or reliable predictions. In the past years, there was not a single year with a full groundwater chemistry analysis, as alot of data was missing for most of the months every year. The absence of data for the year 2013 in the literature collected, shows that there was no monitoring carried out for the whole year. Like modeling, prediction of contaminant plumes requires a huge amount of data.

The prediction of arsenic development was however done based on the graph trends (in appendices). The trends show that the water chemistry will remain the same for some time, provided that the conditions will remain the same. The contaminant concentrations will decline in the future if preventive measures are to be taken to minimize the amount of contaminants introduced into groundwater. These measures would slow down further movement and spreading of the plume.

The movement and location of contaminant plumes can also be done with geoelectrical resistivity imaging, a geophysical method used to estimate resistivity distribution in the earth subsurface.

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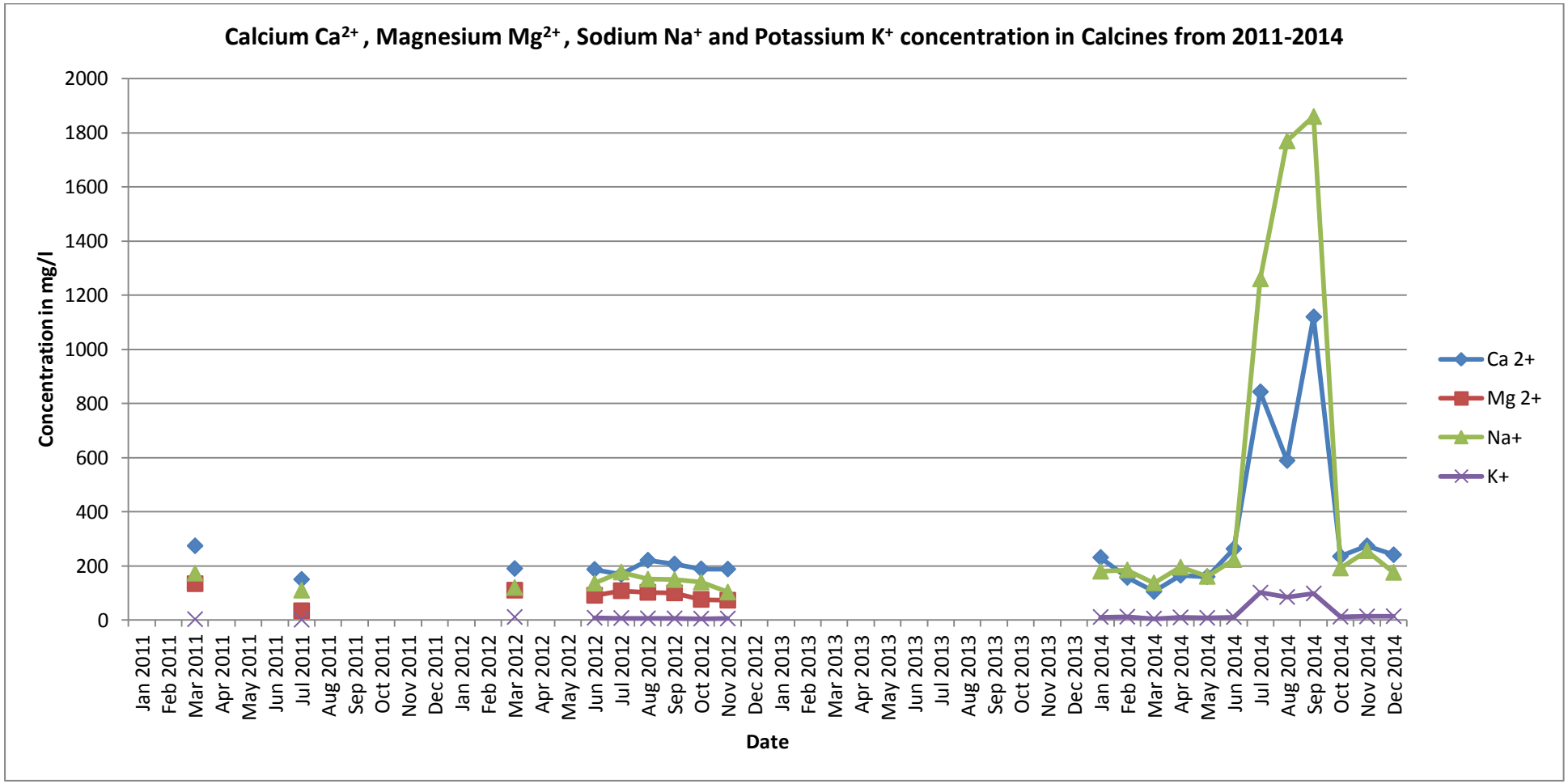
9 List of Figures and Tables

9.1 List of Figures

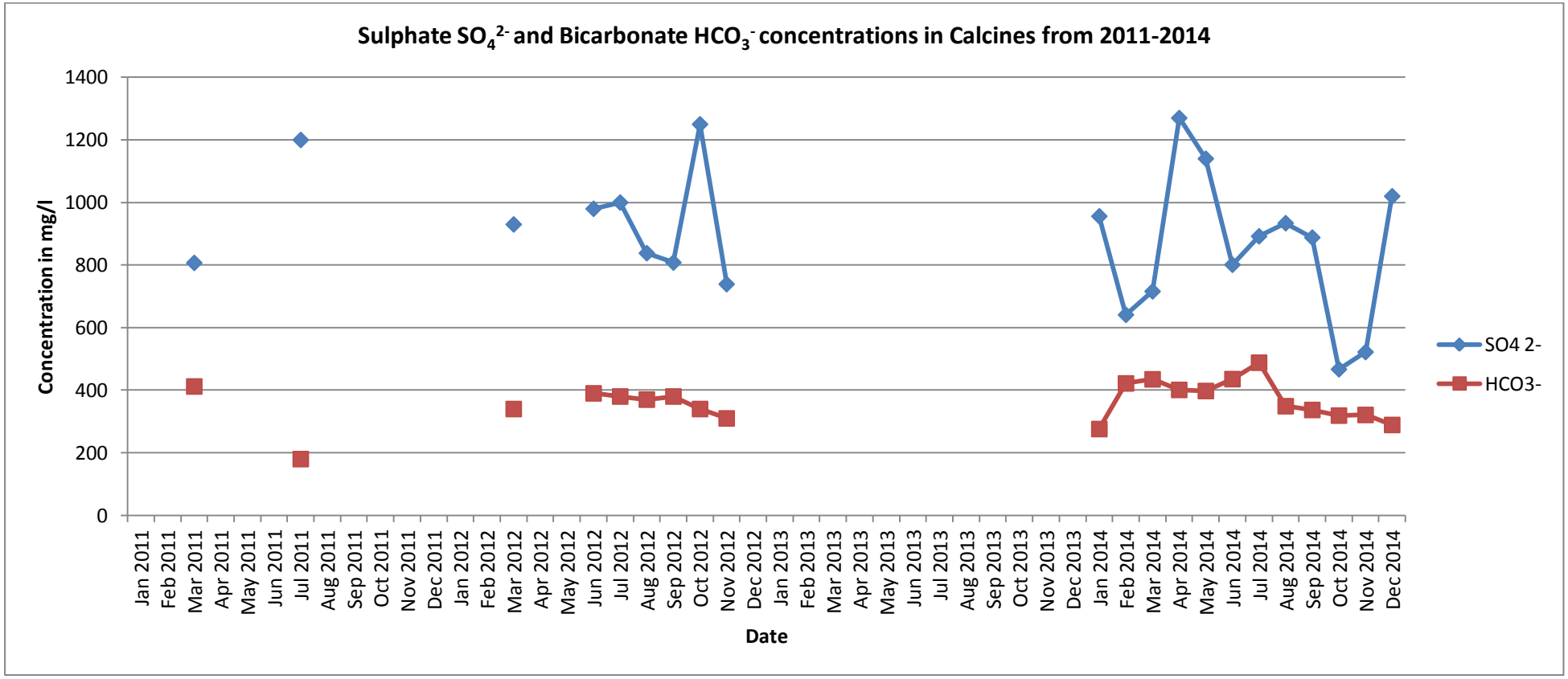
9.2 List of Tables

9.3 List of Appendices

APPENDIX 1: Major cations-Calcine



APPENDIX 2: Major anions I-Calcine



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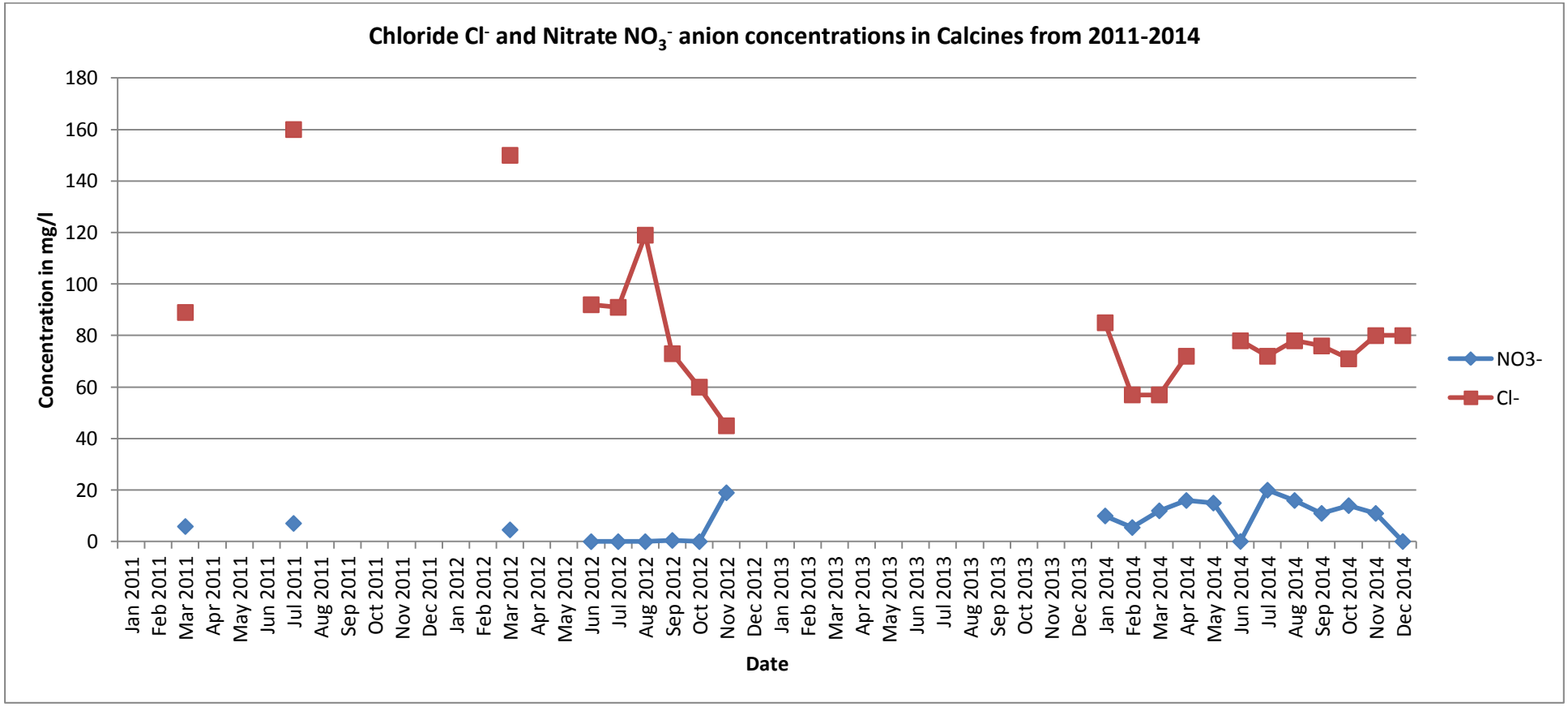
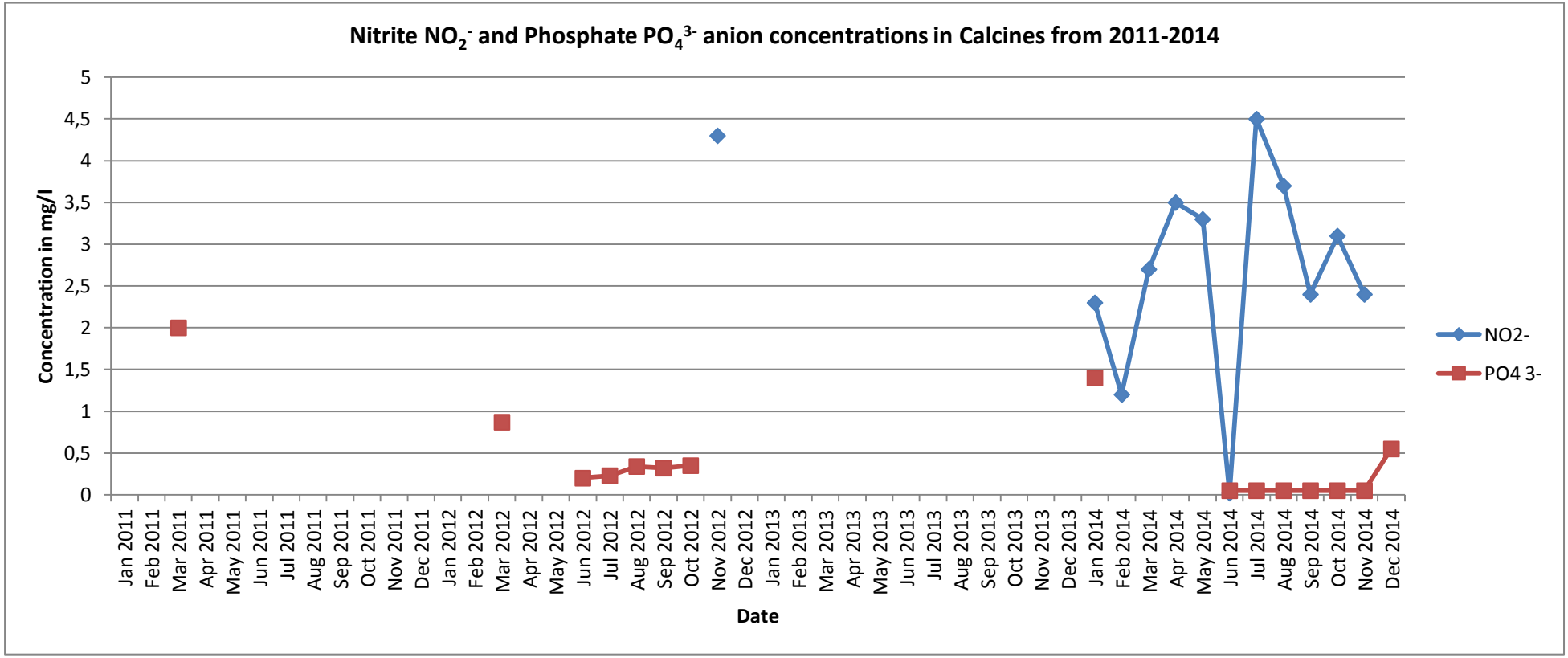


APPENDIX 4: Other anions-Calcine



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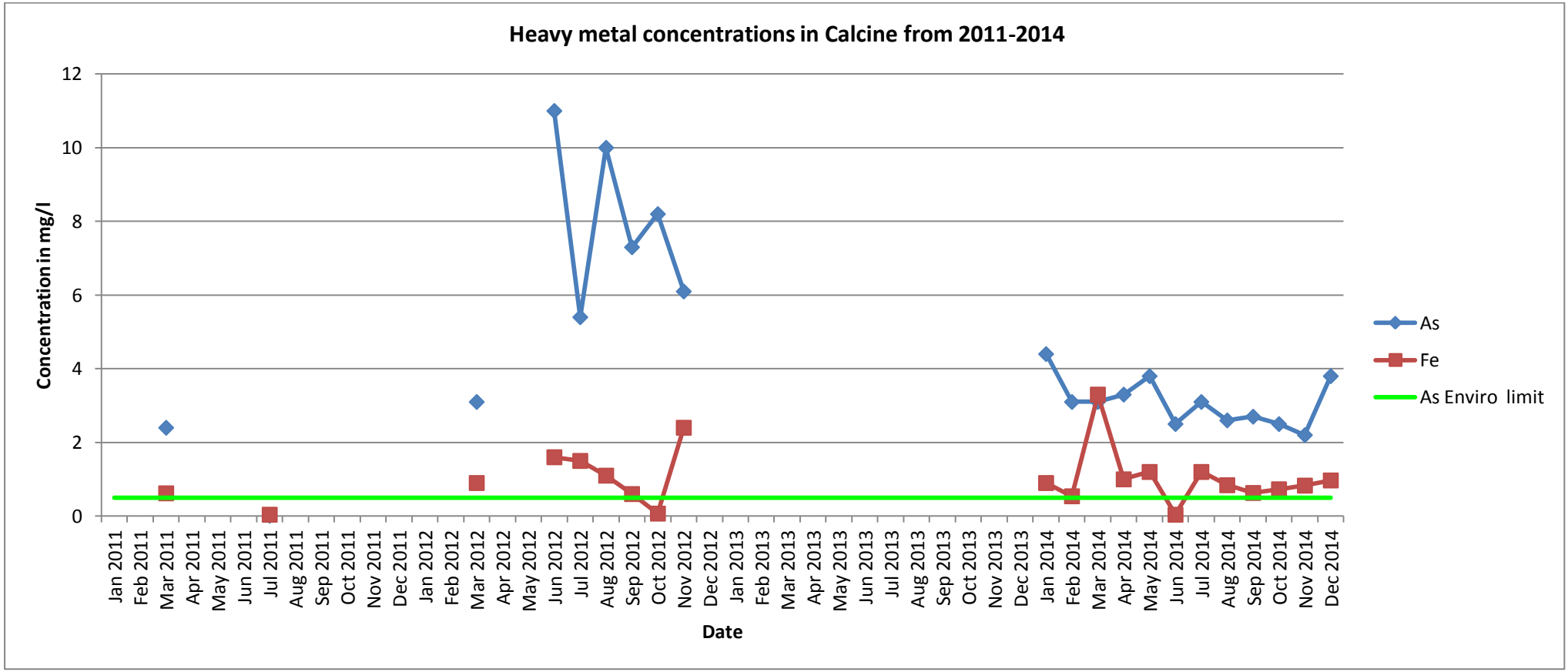
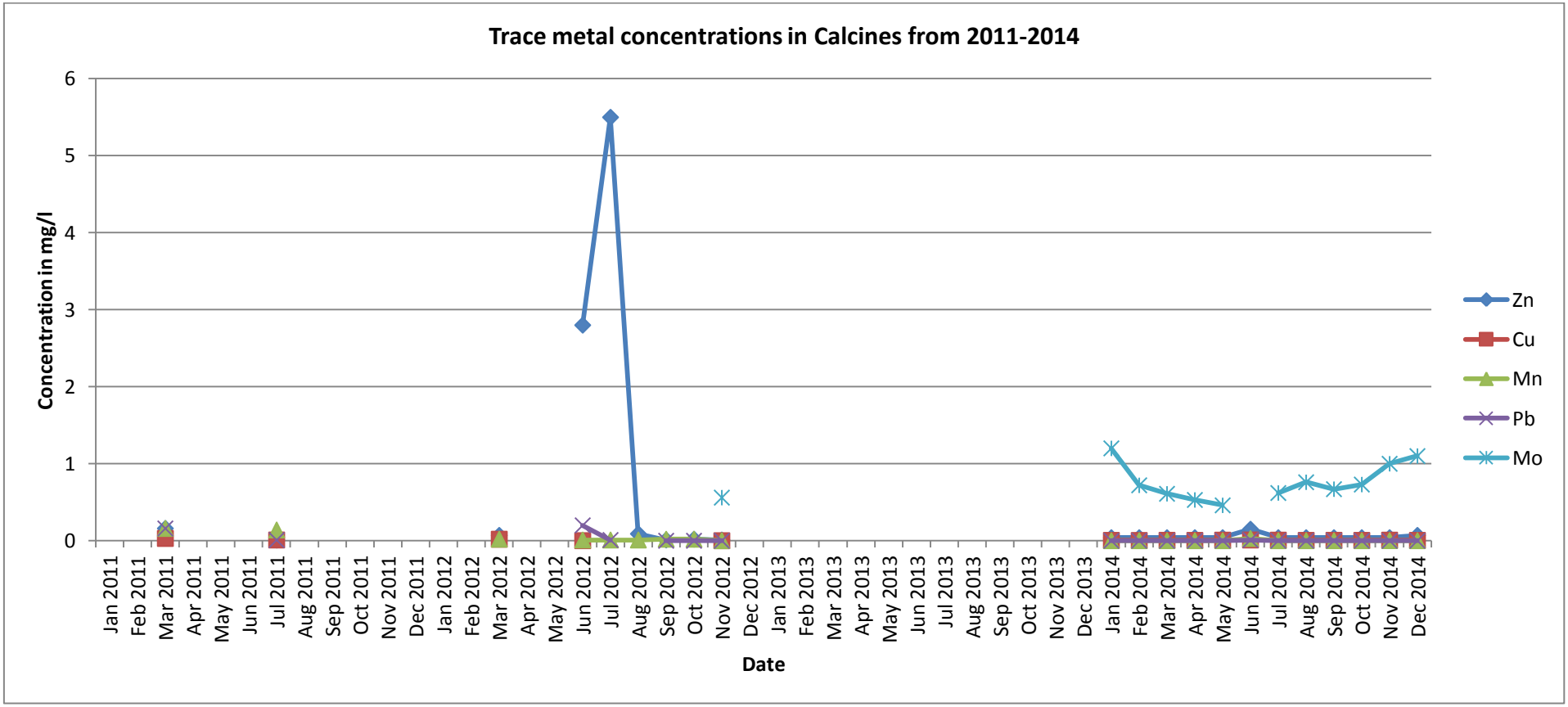
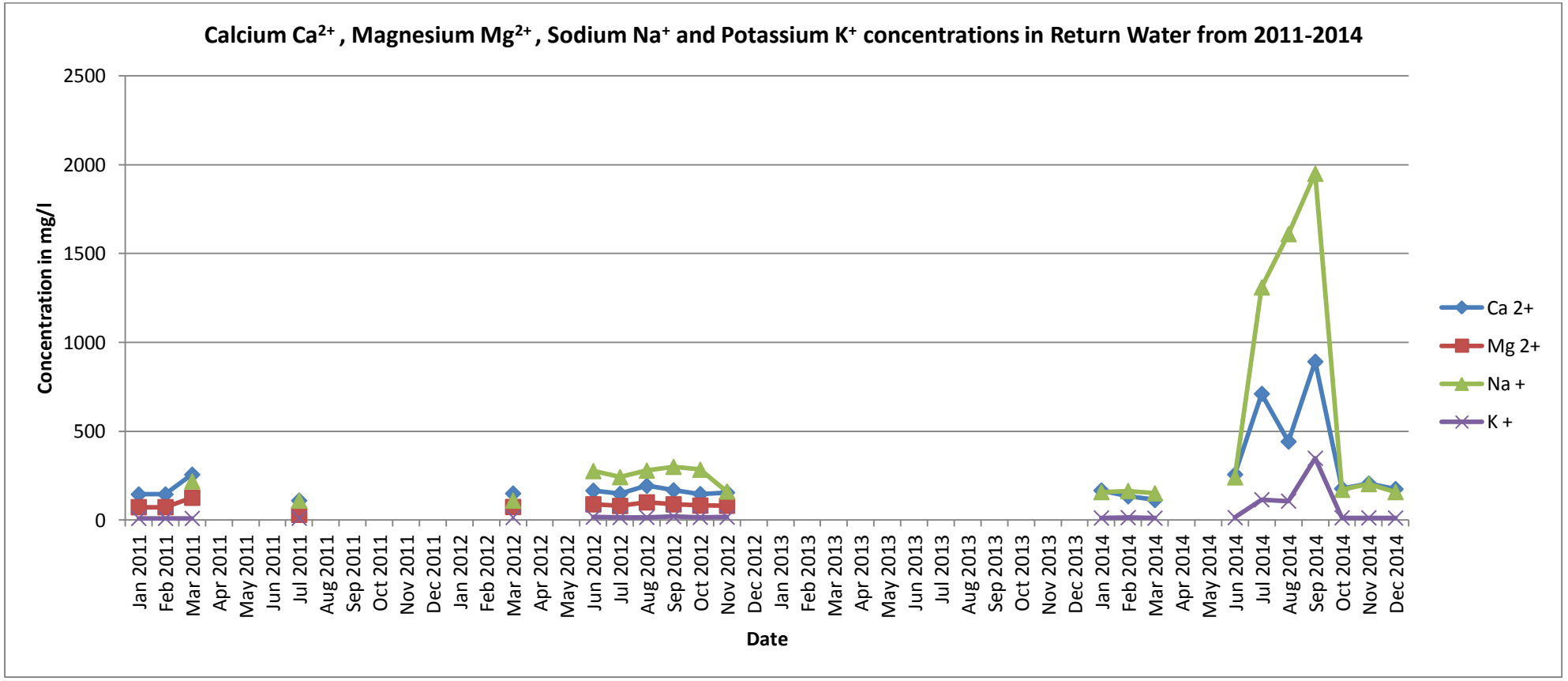


APPENDIX 6: Trace metals-Calcine



APPENDIX 7: Major cations-Return Water



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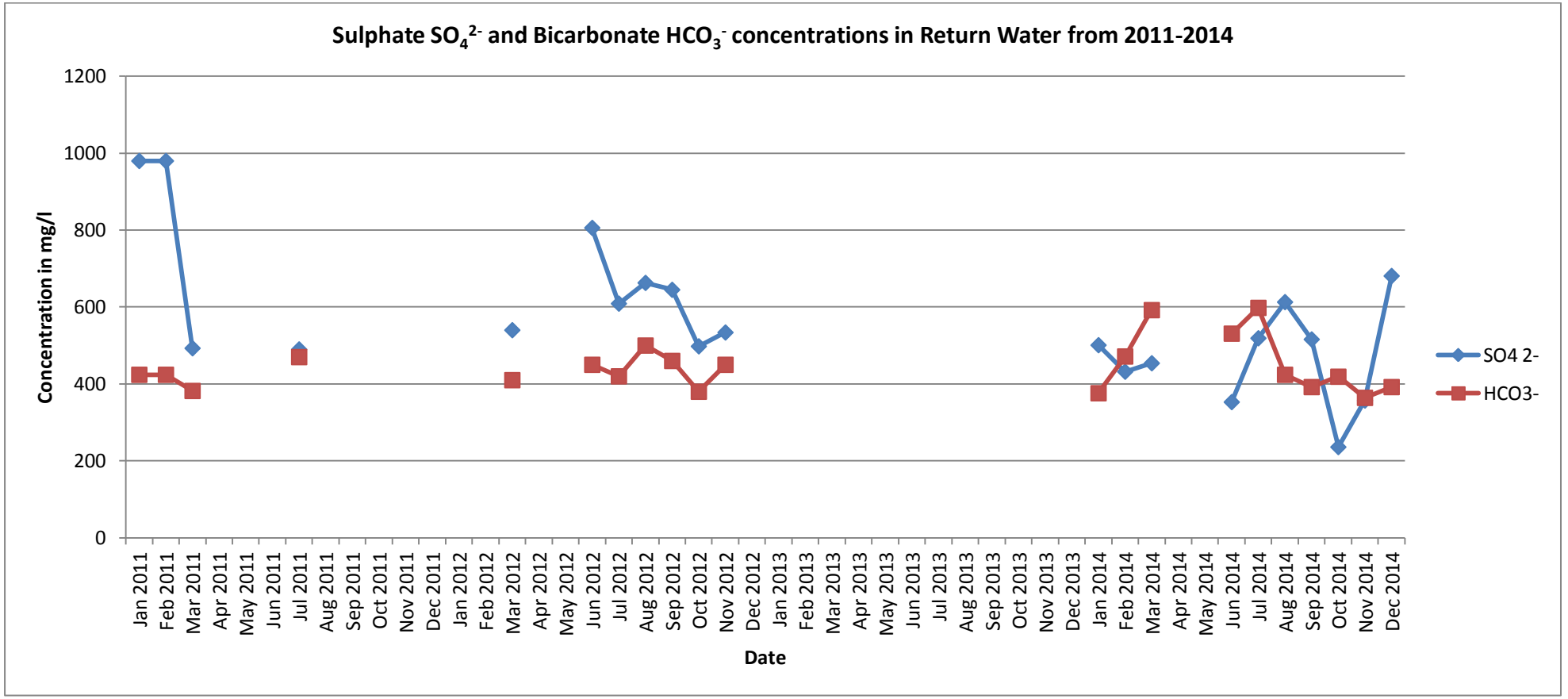

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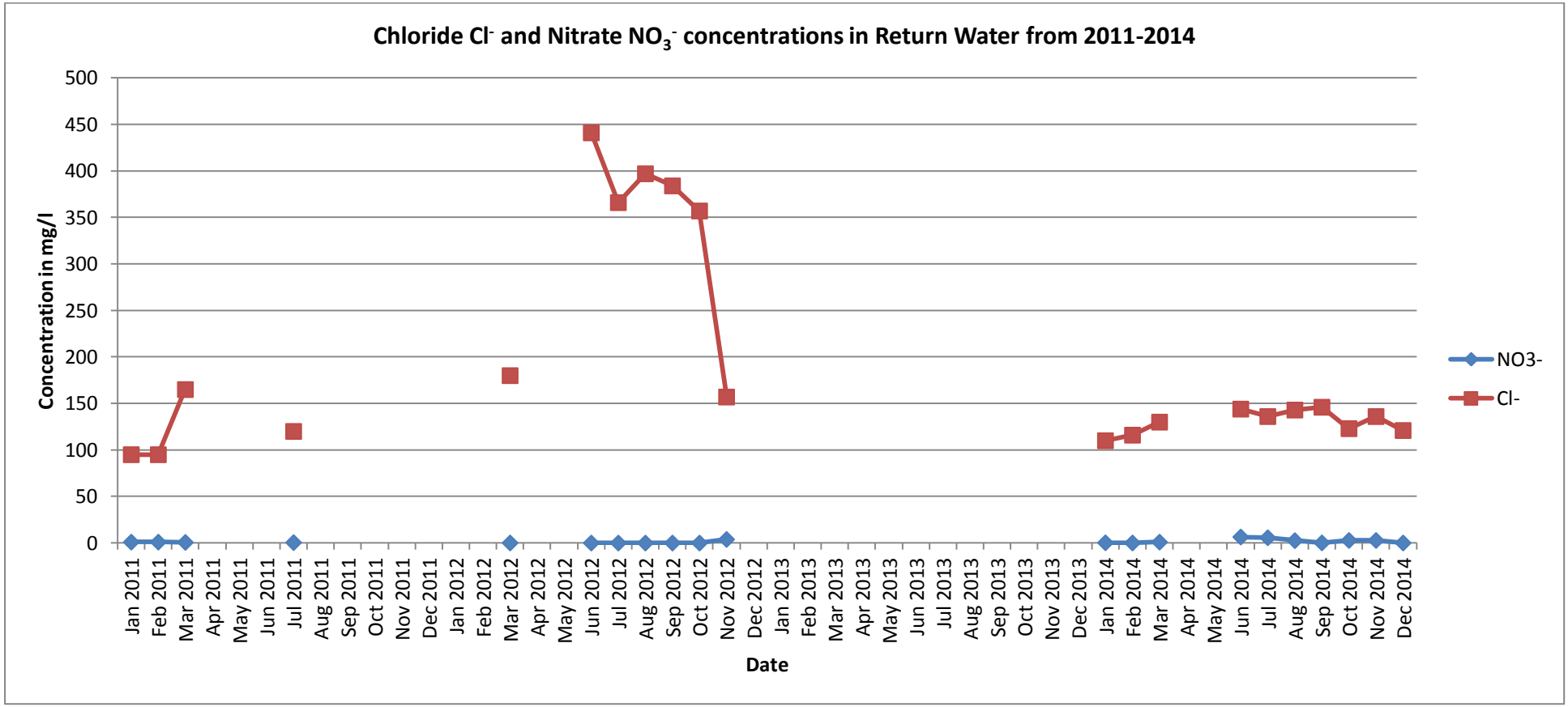
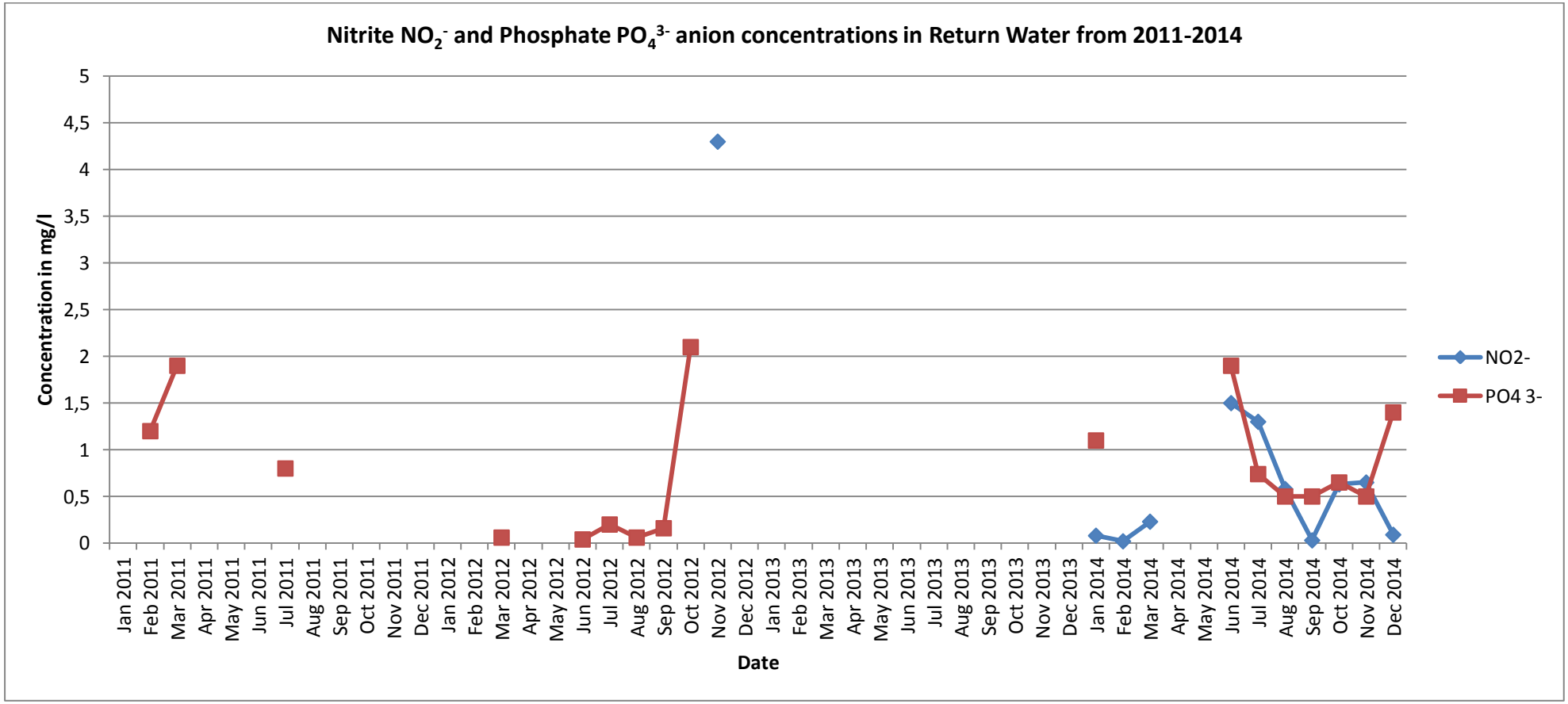
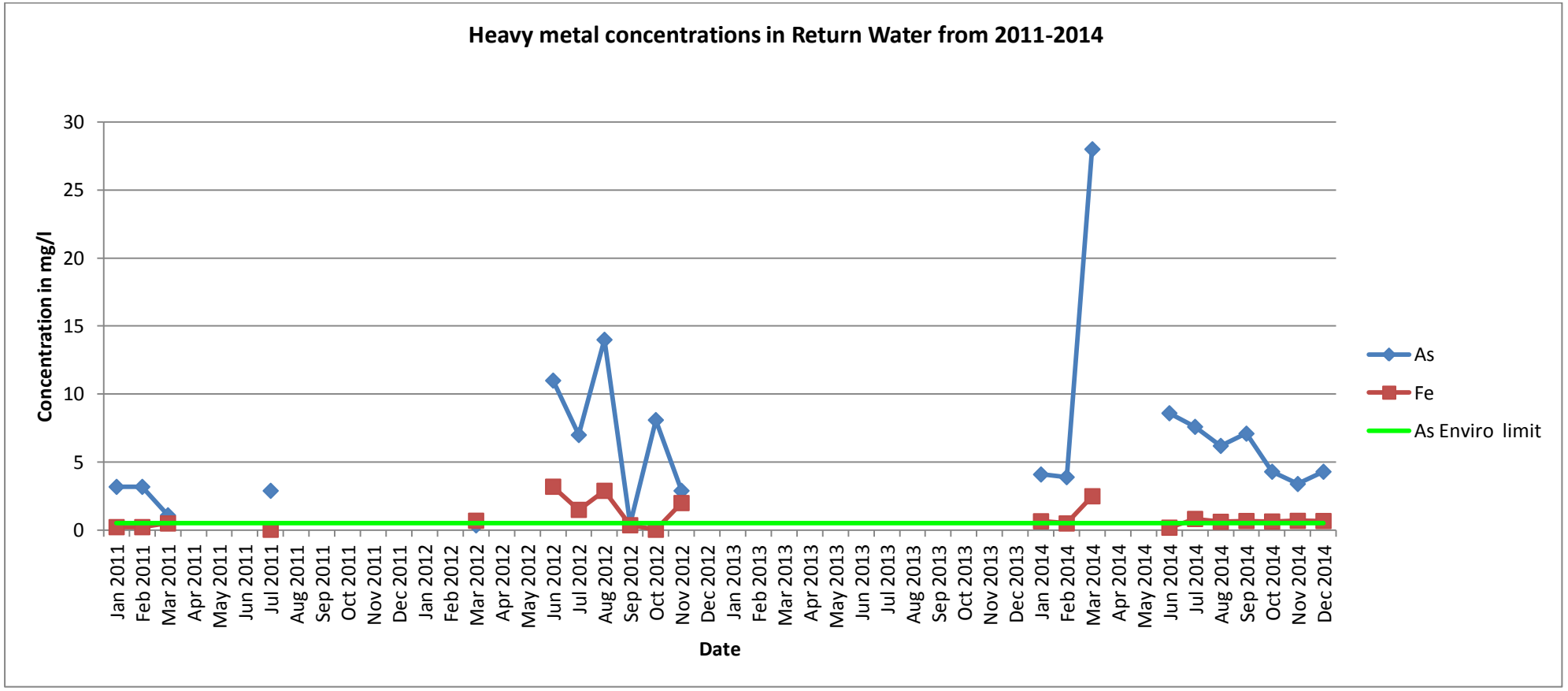


APPENDIX 10: Other anions-Return Water



APPENDIX 11: Heavy metals-Return Water



APPENDIX 12: Trace metals-Return Water